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**(54) Supported catalysts for the polymerization of olefins**

Geträgerte Katalysatoren für die Polymerisation von Olefinen

Catalyseurs supportés pour la polymérisation d'oléfines

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**EP-A- 0 295 312** **EP-A- 0 442 725**  
**EP-A- 0 496 405** **EP-A- 0 546 690**  
**US-A- 4 147 664** **US-A- 5 198 399**

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**EP 0 633 272 B1**

## Description

The present invention relates to a supported catalyst for the polymerization of olefins, the process for the preparation thereof and the use of said supported catalyst in processes for the polymerization of olefins.

Homogeneous catalytic systems for the polymerization of olefins based on coordination complexes of a transition metal such as titanium, zirconium or hafnium with ligands of the cyclopentadienyl type are known. Generally, these catalytic system comprise a soluble cocatalyst, such as the methylalumoxane (MAO).

These homogeneous catalytic systems show many advantages in comparison with traditional heterogeneous catalysts of the Ziegler-Natta type. In particular, they allow a careful control of the stereoregularity degree and type, the molecular weight distribution and comonomer distribution, besides making easier the use of higher  $\alpha$ -olefins, di-olefins and dienes as comonomers. Thus, new polymers or polymers endowed with remarkably improved properties can be obtained.

However, being soluble in the reaction system, these catalytic systems can not easily be utilized in polymerization processes which are not carried out in solution. Furthermore, the polymers obtained by processes using the above mentioned catalysts, are generally not endowed with satisfactory morphological characteristics.

In order to avoid these drawbacks, systems have been suggested based on supporting at least one component of the above mentioned catalysts on insoluble solid supports. In most cases these solid supports consist of inorganic oxides and, in particular, of silica or alumina.

In the prior art, cases are found wherein the opportunity of using supports of the polymeric type is foreseen.

In European patent applications EP-279 863 and EP-295 312 supported homogeneous catalysts comprising methylalumoxane and bis(cyclopentadienyl)zirconium dichloride are described. Besides silica inorganic supports, organic supports consisting of polyethylene or polystyrene have been used. In the preparation of the supported catalysts, use has been made of *n*-decane, which has the function of precipitating the methylalumoxane. These supported catalysts, after a prepolymerization treatment with ethylene in *n*-decane, have been used in the polymerization reaction of ethylene in gas-phase. To attain acceptable results, high amounts of methylalumoxane for each gram of solid support have been used.

In European patent application EP-518 092 catalysts of the type metallocene/alumoxane supported on polypropylene are described. These catalysts have been used in the polymerization reaction of propylene carried out in liquid monomer or in gas phase. Nothing is said about the bulk density of the polymers obtained.

Although these types of catalytic systems supported on polymeric materials are useable in processes carried out in suspension or in gas phase with acceptable yields, however they do not allow polymers endowed with good morphological characteristics to be obtained.

It has now been found by the Applicant that metallocene/alumoxane catalytic systems can be advantageously made heterogeneous by supporting them on functionalised porous organic supports. By this way it is possible to obtain catalysts in form of spherical particles, endowed with acceptable activities, able to produce polymers which duplicate the shape of the catalyst and therefore are endowed with controlled morphology and high bulk density.

Therefore, an object of the present invention is a supported catalyst for the polymerization of olefins comprising:

(A) a porous organic support functionalised with groups having active hydrogen atoms;

(B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur; and

(C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type.

The porosity (B.E.T.) of the organic support is generally higher than  $0.2 \text{ cm}^3/\text{g}$ , preferably higher than  $0.5 \text{ cm}^3/\text{g}$ , more preferably higher than  $1 \text{ cm}^3/\text{g}$ . In particular, supports suitably useable have a porosity comprised between 1 and  $3 \text{ cm}^3/\text{g}$ .

The surface area (B.E.T.) of the organic support is generally higher than  $30 \text{ m}^2/\text{g}$ , preferably higher than  $50 \text{ m}^2/\text{g}$ , more preferably higher than  $100 \text{ m}^2/\text{g}$ . In particular, the surface area can reach values of about  $500 \text{ m}^2/\text{g}$  and over.

The organic support is preferably in form of particles having controlled morphology, in particular microspheroidal morphology with a diameter comprised between about 5 and  $1000 \mu\text{m}$ , preferably between 10 and  $500 \mu\text{m}$ , more preferably between 20 and  $200 \mu\text{m}$ .

Supports which can be used in the catalysts according to the present invention are those polymers, endowed with the above mentioned characteristics regarding the porosity and surface area, which show functional groups having active hydrogen atoms.

Examples of suitable functional groups are hydroxyl groups, primary and secondary amino groups, sulphonic groups, carboxylic groups, amido groups, N-monosubstituted amido groups, sulphonamido groups, N-monosubstituted sulphonamido groups, sulphydril groups, imido groups and hydrazido groups.

The amount of functional groups contained in the supports is generally higher than 0.2 milliequivalents (meq) for each gram of solid support, preferably higher than 0.5 meq for each gram of solid support, more preferably is comprised between 1 and 6 meq for each gram of solid support.

A class of supports particularly suitable for use in the catalysts of the present invention can be obtained from partially cross-linked porous styrenic polymers. These supports can be prepared by copolymerization of styrenic monomers, such as styrene, ethylvinylbenzene, vinyltoluene, methylstyrene and mixtures thereof, with comonomers able to be cross-linked, such as divinylbenzene, divinyltoluene and mixtures thereof. Preferred styrenic polymers are partially cross-linked styrene/divinylbenzene copolymers. Methods for the preparation of these copolymers are described, for example, in USP 4,224,415, the content of which is incorporated in the present description.

Porous polymers of this type can be functionalised by means of known methods. The most common methods to functionalise polystyrene resins are reported in "Comprehensive Pol. Sci., Pergamon Press, pages 82-85 (1989)".

A method for the preparation of alpha-hydroxyalkylated resins is described by I. Fujita et al. in "Separation Science and Technology, 26, 1395-1402, (1991)".

Functionalized porous styrenic polymers useable as supports according to the present invention are, moreover, those which can be directly obtained from the copolymerization of styrenic monomers with comonomers functionalized with groups containing active hydrogens or their precursors. Examples of these polymers are the styrenic copolymers functionalised with hydroxy groups, which are described in the European patent application EP-496 405.

The transition metal of groups IVb, Vb or Vlb of the Periodic Table of the Elements is preferably selected from titanium, zirconium, hafnium and vanadium, more preferably is zirconium.

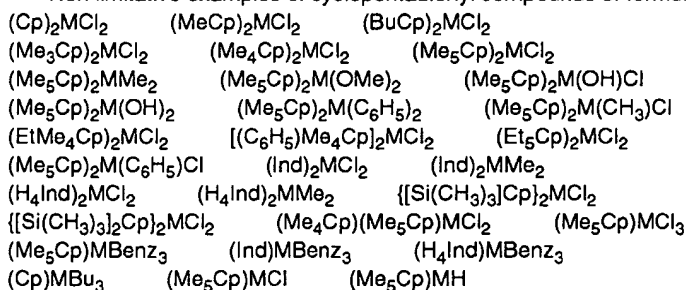
Transition metal compounds useable in the supported catalysts according to the present invention are, for example, the cyclopentadienyl compounds of formula (I):



wherein M is Ti, Zr, Hf or V; the two  $C_5R^1_{5-m}$  groups, are cyclopentadienyl rings equally or differently substituted; substituents  $R^1$ , same or different from each other, are hydrogen, alkyl, alkenyl, aryl, alkaryl or aralkyl radicals containing from 1 to 20 carbon atoms which may also contain Si or Ge atoms or  $Si(CH_3)_3$  groups, or furthermore two or four substituents  $R^1$  of a same cyclopentadienyl ring may form one or two rings having from 4 to 6 carbon atoms;  $R^2$  is a bridging group which links the two cyclopentadienyl rings and is selected among  $CR^3_2$ ,  $C_2R^3_4$ ,  $SiR^3_2$ ,  $Si_2R^3_4$ ,  $GeR^3_2$ ,  $Ge_2R^3_4$ ,  $R^3_2SiCR^3_2$ ,  $NR^1$  or  $PR^1$ , wherein the substituents  $R^3$ , same or different from each other, are  $R^1$  or two or four substituents  $R^3$  may form one or two rings having from 3 to 6 carbon atoms; substituents Q, same or different from each other, are halogen, hydrogen,  $R^1$ ,  $OR^1$ ,  $SR^1$ ,  $NR^1_2$  or  $PR^1_2$ ; m can be 0 or 1; n can be 0 or 1, being 1 if m=1; p can be 2 or 3, preferably it is 3.

In the case of m=0, particularly suitable cyclopentadienyl compounds are those wherein the groups  $C_5R^1_{5-m}$  are selected among cyclopentadienyl, pentamethyl-cyclopentadienyl, indenyl and 4,5,6,7-tetrahydroindenyl groups, and substituents Q are selected among chlorine atoms and  $C_1$ - $C_7$  hydrocarbon groups, preferably methyl groups.

Non limitative examples of cyclopentadienyl compounds of formula (I), wherein m=0, are:



wherein Me=methyl, Et=ethyl, Bu=butyl, Cp=cyclopentadienyl, Ind=indenyl,  $H_4Ind$ =4,5,6,7-tetrahydroindenyl, Benz=benzyl, M is Ti, Zr, Hf or V, preferably is Zr.

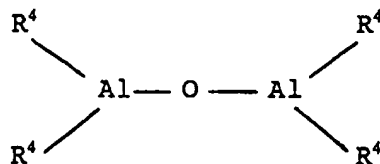
In the case of m=1, particularly suitable cyclopentadienyl compounds are those wherein the groups  $C_5R^1_{5-m}$  are selected among cyclopentadienyl, tetramethyl-cyclopentadienyl, indenyl, 2-methyl-indenyl, 4,7-dimethyl-indenyl, 2,4,7-trimethyl-indenyl, 4,5,6,7-tetrahydroindenyl, 2-methyl-4,5,6,7-tetrahydroindenyl, 4,7-dimethyl-4,5,6,7-tetrahydroindenyl, 2,4,7-trimethyl-4,5,6,7-tetrahydroindenyl or fluorenyl groups,  $R^2$  is a divalent group selected among  $(CH_3)_2Si$ ,  $C_2H_4$  and  $C(CH_3)_2$ , and substituents Q are selected among chlorine atoms and  $C_1$ - $C_7$  hydrocarbon groups, preferably methyl groups.

Non limitative examples of cyclopentadienyl compounds of formula (I), wherein m=1, are:

$\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})_2\text{M Me}_2$      $\text{Me}_2\text{C}(\text{Me}_4\text{Cp})(\text{MeCp})\text{MCl}_2$   
 $\text{Me}_2\text{Si}(\text{Ind})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(\text{Ind})_2\text{M Me}_2$      $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})_2\text{MCl}(\text{OEt})$   
 $\text{C}_2\text{H}_4(\text{Ind})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(\text{Ind})_2\text{MMe}_2$      $\text{C}_2\text{H}_4(\text{Ind})_2\text{M}(\text{NMe}_2)_2$   
 $\text{C}_2\text{H}_4(\text{H}_4\text{Ind})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(\text{H}_4\text{Ind})_2\text{MMe}_2$      $\text{C}_2\text{H}_4(\text{H}_4\text{Ind})_2\text{M}(\text{NMe}_2)\text{OMe}$   
5     $\text{Ph}(\text{Me})\text{Si}(\text{Ind})_2\text{MCl}_2$      $\text{Ph}_2\text{Si}(\text{Ind})_2\text{MCl}_2$      $\text{Me}_2\text{C}(\text{Flu})(\text{Cp})\text{MCl}_2$   
 $\text{C}_2\text{H}_4(\text{Me}_4\text{Cp})_2\text{MCl}_2$      $\text{C}_2\text{Me}_4(\text{Ind})_2\text{MCl}_2$      $\text{Me}_2\text{SiCH}_2(\text{Ind})_2\text{MCl}_2$   
 $\text{C}_2\text{H}_4(2\text{-MeInd})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(3\text{-MeInd})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{Ind})_2\text{MCl}_2$   
 $\text{C}_2\text{H}_4(5,6\text{-Me}_2\text{Ind})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(2,4,7\text{-Me}_3\text{Ind})_2\text{MCl}_2$   
10     $\text{C}_2\text{H}_4(3,4,7\text{-Me}_3\text{Ind})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(2\text{-MeH}_4\text{Ind})_2\text{MCl}_2$   
 $\text{C}_2\text{H}_4(4,7\text{-Me}_2\text{H}_4\text{Ind})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(2,4,7\text{-Me}_3\text{H}_4\text{Ind})_2\text{MCl}_2$   
 $\text{C}_2\text{H}_4(\text{Benz}[e]\text{Ind})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(2\text{-Me-Benz}[e]\text{Ind})_2\text{MCl}_2$   
 $\text{Me}_2\text{Si}(2\text{-MeInd})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(3\text{-MeInd})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(4,7\text{-Me}_2\text{Ind})_2\text{MCl}_2$   
 $\text{Me}_2\text{Si}(5,6\text{-Me}_2\text{Ind})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(2,4,7\text{-Me}_3\text{Ind})_2\text{MCl}_2$   
15     $\text{Me}_2\text{Si}(3,4,7\text{-Me}_3\text{Ind})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(2\text{-MeH}_4\text{Ind})_2\text{MCl}_2$   
 $\text{Me}_2\text{Si}(4,7\text{-Me}_2\text{H}_4\text{Ind})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(2,4,7\text{-Me}_3\text{H}_4\text{Ind})_2\text{MCl}_2$   
 $\text{Me}_2\text{Si}(\text{Flu})_2\text{MCl}_2$      $\text{C}_2\text{H}_4(\text{Flu})_2\text{MCl}_2$   
 $\text{Me}_2\text{Si}(\text{Benz}[e]\text{Ind})_2\text{MCl}_2$      $\text{Me}_2\text{Si}(2\text{-Me-Benz}[e]\text{Ind})_2\text{MCl}_2$  wherein Me=methyl, Cp=cyclopentadienyl, Ind=indenyl, Flu=fluorenyl, Ph=phenyl, H<sub>4</sub>ind=4,5,6,7-tetrahydroindenyl, M is Ti, Zr, Hf or V, preferably is Zr.

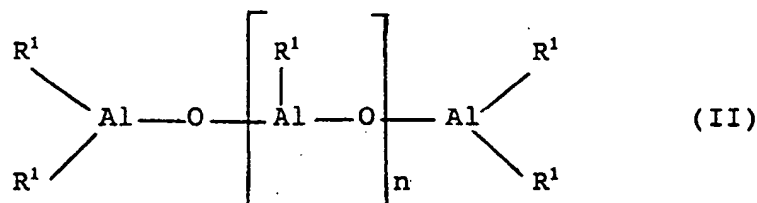
Another type of transition metal compounds useable in the supported catalysts according to the present invention, are the mono-cyclopentadienyl "constrained geometry" compounds described, for example, in European patent applications EP-416 815, EP-420 436 and EP-520 732, the content of which is incorporated in the present description.

Organo-metallic compounds of aluminium useable in the supported catalysts according to the invention are, for example, linear, branched or cyclic alumoxane containing at least one group of the type:

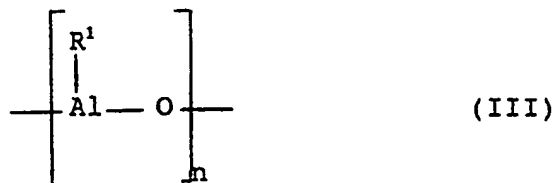


wherein the substituents R<sup>4</sup>, same of different form each other, are defined as R<sup>1</sup> or are a group -O-Al(R<sup>4</sup>)<sub>2</sub>, and optionally some R<sup>4</sup> can be halogen atoms.

In particular, it is possible to use alumoxanes of formula (II):



in case of linear compounds, wherein n is 0 or an integer comprised between 1 and 40, or alumoxanes of formula (III):

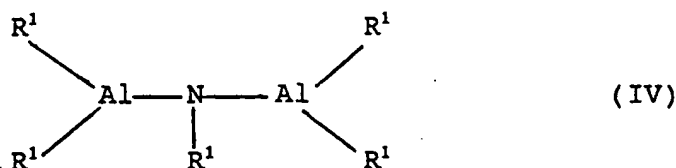


in case of cyclic compounds, wherein n is an integer comprised between 2 and 40. Radicals R<sup>1</sup> are defined as above.

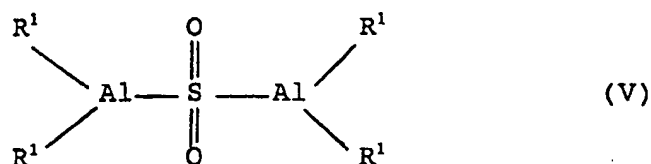
Examples of alumoxanes suitable for use in the supported catalysts of the present invention are those in which radicals  $R^1$  are selected among methyl, ethyl and isobutyl groups, particularly methylalumoxane (MAO) and isobutylalumoxane (TIBAO).

A special class of organo-metallic compounds of aluminium useable in the supported catalysts according to the invention is that of compounds obtainable by reaction of aluminium alkyls or alkylhydrides with water in molar ratio comprised between 1:1 and 100:1 respectively. Compounds of this type are described in European patent application EP-575 875, the content of which is incorporated in the present description.

Moreover, organo-metallic compounds of aluminium useable in the supported catalysts of the invention are those of formula (IV):



or of formula (V):



wherein  $R^1$  is defined as above.

The molar ratio between the aluminium and the transition metal in the supported catalysts of the invention is generally comprised between 10 and 500, preferably between 20 and 200, more preferably between 30 and 100.

The supported catalysts of the present invention can be prepared by contacting the components (A), (B) and (C) among themselves in different sequences.

An advantageous process for the preparation of a supported catalysts according to the present invention comprises contacting in an inert solvent

- (A) a porous organic support functionalised with groups having active hydrogen atoms, and
- (B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur;

thereafter contacting the thus obtained product with

- (C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type;

and finally recovering the supported catalyst by removing the solvent.

Another process for the preparation of a supported catalyst according to the present invention comprises contacting in an inert solvent

- (B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur, and
- (C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type;

thereafter contacting the thus obtained product with

- (A) a porous organic support functionalised with groups having active hydrogen atoms;

and finally recovering the supported catalyst by removing the solvent.

Yet another process for the preparation of a supported catalyst according to the present invention comprises contacting in an inert solvent

- (A) a porous organic support functionalised with groups having active hydrogen atoms, and  
(B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur;

contacting in an inert solvent

- (B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur, and  
(C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type;

thereafter contacting the product obtained by contacting (A) and (B) with the product obtained by contacting (B) and (C); and finally recovering the supported catalyst by removing the solvent.

The above indicated processes for the preparation of the supported catalysts of the invention are conducted at a temperature which is generally comprised between -80 and 100°C.

The organic support can be advantageously pre-contacted with aluminium alkyl compounds of formula (VI):



wherein  $R^5$  is selected among alkyl, alkenyl, aryl, alkaryl and aralkyl radicals containing from 1 to 10 carbon atoms, X is selected among hydrogen and halogen atoms, q is an integer comprised between 1 and 3.

Non limitative examples of aluminum alkyl compounds of formula (VI) are aluminium trialkyls such as trimethylaluminium, triethylaluminium, triisopropylaluminium and triisobutylaluminium; dialkylaluminium halides such as dimethylaluminium chloride, diethylaluminium chloride, diisopropylaluminium chloride and diisobutylaluminium chloride; dialkylaluminium hydrides such as diethylaluminium hydride and diisobutylaluminium hydride; isoprenylaluminium. A preferred aluminium alkyl compound is triisobutylaluminium.

The supported catalysts of the present invention, before being used, can be subjected to a pre-polymerization treatment, by pre-contacting them with small amounts of olefinic monomer.

Therefore, another object of the present invention is a supported and pre-polymerized catalyst for the polymerization of olefins obtainable by subjecting a supported catalyst according to the present invention to a pre-polymerization treatment with at least one olefinic monomer.

The pre-polymerization treatment is generally carried out in an inorganic solvent. The amount of polymer produced in this step is generally comprised between 0.5 and 10 parts by weight with respect to the weight of the supported catalyst used.

The pre-polymerization can be advantageously carried out in the presence of aluminium alkyl compounds of formula (VI):



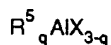
wherein  $R^5$ , X and q are defined as above, or in the presence of organo-metallic compounds of aluminium (B) as above described, in particular alumoxanes. Aluminium alkyl compounds of formula (VI) are preferred.

The supported catalysts of the present invention are useable in the homo- or co-polymerization reactions of olefins.

Therefore, a further object of the present invention is a process for the homo- or co-polymerization of olefins comprising the polymerization reaction of one or more olefinic monomers in the presence of a supported catalyst as above described.

Still another object of the present invention is a process for the homo- or co-polymerization of olefins comprising the polymerization reaction of one or more olefinic monomers in the presence of a supported and pre-polymerized catalyst as above described.

Before the use, the supported catalysts of the invention and, in particular, those which are not pre-polymerized, can be advantageously pre-contacted with alkyl aluminium compounds of formula (VI):



(VI)

wherein  $R^5$ , X and q are defined as above, or with organo-metallic compounds of aluminium (B) as above described, in particular alumoxanes. Aluminium alkyl compounds of formula (VI) are preferred.

The supported catalysts according to the present invention can be suitably used for the homopolymerization of ethylene and, in particular, for the preparation of HDPE.

Moreover, the supported catalysts of the invention can be suitably used for the copolymerization of ethylene with olefin comonomers and, in particular for the preparation of LLDPE.

The obtained LLDPE copolymers have a content of ethylene units generally comprised between 80 and 99% by mole. Their density is generally comprised between 0.87 and 0.95 cc/g and they are characterized by an uniform distribution of the comonomeric units within the polymeric chain.

Olefins which can be suitably used as comonomers in the above said ethylene copolymers are alpha-olefins of formula  $CH_2=CHR$ , wherein R is a linear or branched or cyclic radical containing from 1 to 20 carbon atoms, as well as cycloolefins.

Non-limitative examples of these olefins are propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, alkylcyclohexene, cyclopentene, cyclohexene, norbornene, 4,6-dimethyl-1-heptene.

The above ethylene copolymers can also contain small amounts of units deriving from polyenes, in particular from dienes, conjugated or not, linear or cyclic, such as, for example, 1,4-hexadiene, isoprene, 1,3-butadiene, 1,5-hexadiene, 1,6-heptadiene.

The ethylene copolymers contain units deriving from olefins of formula  $CH_2=CHR$ , from cycloolefins and/or from polyenes in amounts generally comprised from 1% to 20% by mole.

Another use of interest for the supported catalysts of the present invention is for the preparation of elastomeric copolymers of ethylene with  $\alpha$ -olefins of formula  $CH_2=CHR$ , wherein R is an alkyl radical containing from 1 to 10 carbon atoms, optionally containing lower proportions of units deriving from a polyene.

Saturated elastomeric copolymers obtained with the supported catalysts of the invention generally contain from 15% to 85% by mole of ethylene units, the rest being constituted of units of one or more alpha-olefins and/or of one non-conjugated diolefin able to cyclopolymerize.

Unsaturated elastomeric copolymers contain, besides units deriving from the polymerization of ethylene and alpha-olefins, also lower proportions of unsaturated units deriving from the co-polymerization of one or more polymers. The content of unsaturated units is generally comprised between 0.1% and 5% by weight and, preferably, is comprised between 0.2 and 2% by weight.

The elastomeric copolymers of ethylene obtainable with the supported catalysts of the invention are characterized by valuable properties such as low content of ashes and a uniform distribution of the comonomers in the polymeric chain.

Alpha-olefins which can be suitably used as comonomers in the above said elastomeric ethylene copolymers are, for example, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene.

As non conjugated olefins able to cyclopolymerize, 1,5-hexadiene, 1,6-heptadiene, 2-methyl-1,5-hexadiene can be used.

Polyenes which can be used as comonomers are those comprised in the following classes:

- non-conjugated diolefins capable of cyclopolymerization such as, for example, 1,5-hexadiene, 1,6-heptadiene, 2-methyl-1,5-hexadiene;
- dienes capable of giving unsaturated monomeric units, in particular conjugated dienes such as, for example, butadiene and isoprene; linear non-conjugated dienes such as, for example, trans 1,4-hexadiene, cis 1,4-hexadiene, 6-methyl-1,5-heptadiene, 3,7-dimethyl-1,6-octadiene, 11-methyl-1,10-dodecadiene; monocyclic diolefins such as, for example, cis-1,5-cyclooctadiene and 5-methyl-1,5-cyclooctadiene; dicyclic diolefins such as for example 4,5,8,9-tetrahydroindene and 6 and/or 7-methyl-4,5,8,9-tetrahydroindene; alkenyl or alkyliden norbornenes such as for example 5-ethyliden-2-norbornene, 5-isopropyliden-2-norbornene, exo-5-isopropenyl-2-norbornene; polycyclic diolefins such as for example, dicyclopentadiene, tricyclo-[6.2.1.0<sup>2,7</sup>]-4,9-undecadiene and the 4-methyl-derivative thereof.

Still another use of interest of the supported catalysts of the invention is for the homo- or co-polymerization of propylene and alpha-olefins such as, for example, 1-butene. Depending on the catalytic system used, polymers showing isotactic, syndiotactic or atactic structure can be obtained.

A further use of interest of the supported catalysts of the invention is for the preparation of polymers of cycloolefins. Monocyclic or polycyclic olefinic monomers can be either homopolymerized or copolymerized also with non cyclic

olefinic monomers. Not limitative examples of cyclo-olefinic polymers which can be prepared with the supported catalysts of the invention are described in European patent applications EP-501 370 and EP-407 870, the content of which is incorporated in the present description.

The polymerization processes which make use of the supported catalysts of the present invention can be carried out in liquid phase, in the presence or not of an inert hydrocarbon solvent. The solvent can be aliphatic such as, for example, propane, hexane, heptane, isobutene, cyclohexane, or aromatic such as, for example, toluene.

The polymerization processes which make use of the supported catalysts of the present invention can be advantageously carried out in gas phase.

The polymerization temperature is generally comprised between 0°C and 250°C. In particular, in the processes for the preparation of HDPE and LLDPE, the polymerization temperature is generally comprised between 20°C and 150°C and, particularly, between 40°C and 90°C. In the processes for the preparation of elastomeric copolymers the polymerization temperature is generally comprised between 20°C and 100°C and, particularly, between 30°C and 80°C.

The molecular weight of the copolymers can be varied merely by varying the polymerization temperature, the type or the concentration of the catalytic components or by using molecular weight regulators such as, for example, hydrogen.

The molecular weight distribution can be varied either using mixtures of different metallocenes, or carrying out the polymerization in more steps which differ in the polymerization temperature and/or in the concentrations of the molecular weight regulator.

Polymerization yields depend on the purity of the metallocene component of the catalyst. Therefore, the metallocene compounds can be used in the supported catalysts of the invention either as such, or they can be subjected to purification treatments.

The polymers obtainable with the supported catalysts of the present invention are endowed with good morphological characteristics and can be obtained in form of spherical particles having diameters which can be comprised between 100 and 3000 µm, depending on the catalyst and on the polymerization conditions used.

The following examples are given to illustrate and not to limit the invention.

#### CHARACTERIZATIONS

The presence of functional groups on the supports was confirmed by I.R. analysis. The quantitative determination of the functional groups containing active hydrogen atoms was carried out by gas-volumetric measurement during the reaction of the supports with aluminium triethyl.

The porosities and surface areas were determined by nitrogen adsorption according to the method B.E.T. using an instrument SORPTOMATIC 1900 by Carlo Erba, as well as by mercury porosimetry by means of a POROSIMETER 2000 by Carlo Erba.

The intrinsic viscosities (I.V.) were measured in tetrahydronaphthalene at 135°C.

The Differential Scansion Calorimetry measurements were carried out on an instrument DSC-7, of Perkin Elmer Co. Ltd., according to the following method. About 10 mg of sample were heated at 180°C with a scanning speed equal to 10°C/min. The sample was kept at 180°C for 5 minutes and thereafter cooled with a scanning speed equal to 10°C/min. Thereafter, a second scanning was carried out according to the same modalities of the first one. The values reported are those obtained in the second scanning.

The contents of the comonomer units in the copolymers were determined by I.R. analysis.

The absolute densities of the polymers were determined by density gradient columns according to the ASTM method D-1505.

The tamped bulk density (T.B.D.) and the poured bulk density (P.B.D.) were determined according to the method DIN-53194.

#### PREPARATION OF THE CATALYTIC COMPONENTS ETHYLENE-BIS(INDENYL)ZIRCONIUM DICHLORIDE

##### (A) Preparation of 1,2-bisindenylethane

The preparation described in J. Ewen, J. Am. Chem. Soc., 1987, 109,6544, Suppl. mat. was followed.

Into a 2 litre two-necked round-bottomed flask, 50 g of indene (437 mmol) were dissolved under inert atmosphere with 500 ml of tetrahydrofuran and were cooled to -78 °C. By slow dropping (1 hour) 175 ml of n-butyllithium (2.5 M in hexane, 437.5 mmol) were added. The mixture was allowed to heat up to room temperature and was kept under stirring for 4 hours. It was cooled to -78 °C and 40.42 g of dibromoethane (215 mmol) dissolved in 100 ml of tetrahydrofuran were dropped (within 20 minutes). After the end of the addition, the temperature was raised to 50 °C, the whole was kept under stirring for 12 hours, then was cooled down to room temperature and 20 ml of water were added. The organic phase was dried and the residue was extracted with pentane. By evaporation under vacuum 28.65 g of product



were obtained (yield= 51.6%).

#### (B) Preparation of ethylene-bis(indenyl)zirconium dichloride

Into a 250 ml two-necked round-bottomed flask provided with cooler, 8 g (31 mmol) of 1,2-bisindenylethane and 100 ml of anhydrous tetrahydrofuran were introduced, thus obtaining a yellow solution. After cooling to -78 °C, 40 ml of butyllithium (1.6 M in hexane, 64 mmol) were added dropwise, thus obtaining a precipitate which by heating dissolved again thus giving a reddish-yellow solution. Into a 250 ml four-necked round-bottomed flask, provided with cooler, 8.67 g of  $ZrCl_4$  (37.2 mmol) were introduced; this was cooled to -196 °C, and in this 50 ml of tetrahydrofuran were condensed (strongly exothermic reaction), the mixture was allowed to heat up to room temperature and thereafter it was heated under reflux for 40 minutes. At room temperature and while stirring, the solution of the lithium salt of bisindenylethane was added to the solution of the adduct  $ZrCl_4/THF$  and was kept stirred for 20 hours in the dark. At 0 °C gaseous HCl was bubbled in, thus obtaining a yellow solution together with a precipitate of the same colour. The solution was concentrated by evaporating under vacuum part of the solvent, was cooled to -20 °C and filtered off. The precipitate was further purified by extraction with dichloromethane, thus obtaining 2.3 g (14.7%) of product.

#### ETHYLENE-BIS(4,7-DIMETHYL-INDENYL)ZIRCONIUM DICHLORIDE

##### (A) Preparation of 4,7-dimethylindene

The synthesis was carried out according to the method described in "Organometallics, 1990, 9, 3098" (yield 54% from p-xylene).

##### (B) Preparation of 1,2-bis(4,7-dimethyl-3-indenyl)ethane

38.2 g (265 mmol) of 4,7-dimethylindene were dissolved in 350 ml of tetrahydrofuran and the temperature of the solution was raised to 0 °C. Thereafter, 165 ml of n-butyl-lithium (1.6 M in hexane, 264 mmol) were added dropwise over 2.5 hours. After having allowed the whole to again reach room temperature and whilst stirring for 4 hours, a purple-red solution of 4,7-dimethylindenyllithium was obtained. This solution was cooled to -70 °C and treated, dropwise for 35 minutes, with 25.3 g of 1,2-dibromethane (135 mmol) in 15 ml of tetrahydrofuran. After the temperature was raised again to room temperature, a light yellow solution was obtained to which water was added. The organic phase was collected and dried on  $Na_2SO_4$ . The solvent was then evaporated under vacuum and 20 g of product (yield 48%) were obtained.

##### (C) Preparation of *rac* - and *meso* -ethylene-bis(4,7-dimethyl-1-indenyl)zirconium dichloride

A suspension of 10 g of 1,2-bis(4,7-dimethyl-3-indenyl)ethane (31.8 mmol) in 80 ml of tetrahydrofuran was added through a small tube to a solution of 2.82 g of KH (70.3 mmol) in 160 ml of tetrahydrofuran, kept under stirring. After the formation of hydrogen ceased, the resulting brown solution was separated from the excess KH. This solution and a solution of 12 g of  $ZrCl_4(THF)_2$  (31.8 mmol) in 250 ml of tetrahydrofuran were added, dropwise, over 3 hours, by means of a small tube, into a round bottomed flask containing 50 ml of tetrahydrofuran kept under rapid stirring.

A yellow solution and a precipitate were formed. After removal of the solvent under vacuum, the orange-yellow residue (mixture of *racemo* and *meso* isomers in the ratio 2.33:1 at the  $^1H$ -NMR analysis) was subjected to extraction with  $CH_2Cl_2$  until all the orange product was completely dissolved. The yellow solid (1.7 g) resulted in being a single stereoisomer, that is the *meso* (yield 11.3%). After evaporation of  $CH_2Cl_2$  from the orange solution, 4.9 g of an orange solid corresponding to a mixture of 93.7% *racemo* and 6.3% *meso* isomers (Yield 32.5%) was obtained. This solid was then recrystallized from toluene at -20 °C.

#### ETHYLENE-BIS(4,5,6,7-TETRAHYDROINDENYL)ZIRCONIUM DICHLORIDE

It was prepared according to the method described in "H.H. Brintzinger et al., J. Organomet. Chem., 288, p.63 (1985)".

#### METHYLALUMOXANE (MAO)

A commercial product (Schering, MW 1400) was used in a 30% b.w. toluene solution. After having removed the volatile fractions under vacuum, the vitreous material was ground up to obtain a white powder which was further treated under vacuum (0.1 mmHg) for 4 hours at a temperature of 40 °C. The powder thus obtained showed good flowability

properties.

### EXAMPLE 1

#### 5 Preparation of a polystyrenic resin

Into a 30 litre glass reactor, equipped with thermometer, reflux condenser, blade stirrer and thermoregulation system, an aqueous solution consisting of:

- 10
- 11 l. of distilled water
  - 400 ml of a ROAGIT SVM (Rohm) 5% b.w. solution in water;
  - 55.5 g of PROLIT C10 (Caffaro);
  - 11 g of sodium chloride

15 was introduced under nitrogen atmosphere.

The whole was stirred (350 r.p.m.) at room temperature for 1 hour; thereafter an organic solution consisting of:

- 20
- 5.55 l. n-octane;
  - 1.85 l. of toluene;
  - 1.55 l. of styrene;
  - 2.55 l. of 64% of divinylbenzene in ethylvinylbenzene;
  - 74 g of 75% dibenzoylperoxide in water

was introduced.

25 The temperature of the reactor was raised to 80 °C over 1 hour, maintained for 8 hours, then cooled again to room temperature. The product obtained was subjected to repeated washing with distilled water, extraction with methanol at 50 °C and, subsequently, drying at 100 °C and 1 mmHg of residual pressure. 2.7 Kg of product showing microspheroidal morphology was obtained. The product has the following characteristics:

- 30
- Surface area: 370 m<sup>2</sup>/g (B.E.T.), 126 m<sup>2</sup>/g (Hg);
  - Porosity: 1.74 ml/g (B.E.T.), 1.92 ml/g (Hg);
  - Average radius of pores: 94 Å (B.E.T.), 305 Å (Hg);

35

Particle size distribution (P.S.D.):	
0.8%	300µm;
2.2%	300-250 µm;
7.0%	250-180µm;
10.5%	180-150µm;
73.2%	150-106 µm;
5.5%	106-75 µm;
0.8%	75 µm.

40

45

#### Preparation of a functionalized polystyrenic support

##### (A) Acylation

50 Into a 750 ml glass reactor, provided with thermometer, reflux condenser, blade stirrer and thermoregulation system, 300 ml of carbon sulphide and 30 g of the polystyrenic resin were introduced under a nitrogen atmosphere. After having thermostatted at the temperature of 12 °C, 66 g (0.49 mol) of previously milled AlCl<sub>3</sub> and thereafter 32 ml of freshly distilled CH<sub>3</sub>COCl were added over 1 hour. The temperature was then raised to 25 °C and the whole was kept stirred for 6 hours. The mixture was then transferred into a 3 litre round-bottomed flask, kept stirred, containing a mixture of about 1 Kg of milled ice and 300 ml of HCl (37%) and was stirred for 30 minutes. The resin recovered after filtration was subjected to repeated washing with distilled water, then with acetone and finally with methanol. After drying, 34 g of product showing microspheroidal morphology was recovered. The I.R. spectrum showed a band centered at 1685 cm<sup>-1</sup> attributable to the carbonyl groups.

55

**(B) Reduction**

Into a 500 ml glass reactor provided with thermometer, reflux condenser, blade stirrer, 15.2 g of the acylated resin obtained at point (A), 100 ml of dioxane, 100 ml of distilled water and 15 g of  $\text{NaBH}_4$  were introduced. The mixture was kept stirred at a temperature of 25 °C for 50 hours and, after addition of further 4 g of  $\text{NaBH}_4$  was kept stirred for further 70 hours. The resin recovered after filtration was subjected to repeated washing with distilled water, then with acetone and finally with methanol. After drying, 13.4 g of product showing microspheroidal morphology were recovered. The I. R. spectrum showed a widened band centered at  $3440\text{ cm}^{-1}$  attributable to the hydroxyl groups, while the band at  $1685\text{ cm}^{-1}$  of the carbonyl appeared very reduced in comparison with that of the resin of point (A). The content of hydroxyl groups, determined by gas-volumetric titration with aluminium triethyl, is of 3.3 meq per gram of resin.

**EXAMPLE 2****(A) Preparation of a supported catalyst**

Into a 350 ml glass reactor, provided with thermometer, reflux condenser, blade stirrer and thermoregulation system, 100 ml of anhydrous toluene and 5.24 g of the resin obtained in example 1(B) were introduced. The mixture, thermostatted at 0 °C and kept stirred, was added over 40 minutes with 30 ml of a 1 M toluene solution of methylalumoxane (MAO). The mixture was reacted at a temperature of 0 °C for 1 hour, then at a temperature of 30 °C for 1 hour, thereafter at a temperature of 80 °C for 4 hours. After having cooled to 25 °C, 50 ml of a toluene solution containing 221.2 mg of ethylene-bis(indenyl)zirconium dichloride was added over 55 minutes. The temperature was raised to 30 °C and the whole was kept stirred for 2 hours. A reddish solution was obtained which was allowed to decant, thus obtaining a precipitate and a colourless solution which was removed by drainage. The precipitate was repeatedly washed with anhydrous toluene and then dried under vacuum. 8 g of product showing microspheroidal morphology was recovered, having the following composition: Zr= 0.38%, Cl=0.60%, Al=9.8%.

**(B) Pre-polymerization**

Into a 350 ml glass reactor, provided with thermometer, reflux condenser, blade stirrer and thermoregulation system, 150 ml of anhydrous hexane, 1.145 g of the catalyst obtained in example 2(A) and 2 ml of a heptane solution containing 5 mmol of aluminium triisobutyl (TIBAL) were introduced under anhydrous nitrogen atmosphere. The mixture was thermostatted at 35 °C and kept stirred for 15 minutes. Thereafter ethylene was supplied at a pressure of 30 mmHg for 90 minutes. After having removed the solvent by evaporation under vacuum, 5.8 g of a pre-polymer showing microspheroidal morphology was recovered.

**EXAMPLE 3****Ethylene/1-butene copolymerization**

Into a 1.35 litre steel autoclave, provided with stirrer, manometer, temperature indicator, supplying system for the catalyst, feeding lines of monomers and thermostat, purified by washing with propane at 70 °C, 640 ml of propane and the amounts of 1-butene, ethylene and hydrogen indicated in Table 1 were introduced at room temperature. The suspension of the catalyst was prepared as follows. The solid catalyst of example 2(A) and a solution of triisobutyl aluminium (TIBAL) in 10 ml of hexane was introduced into a dropping funnel. After 5 minutes at the temperature of 20 °C, the suspension was injected into the autoclave under ethylene pressure. The temperature then was brought over 5 minutes to the value requested for the polymerization and kept constant for the polymerization time. The total pressure was kept constant by feeding an ethylene/1-butene mixture. The reaction was then interrupted by quick degassing of monomers and the polymer obtained was dried in oven at 60 °C under nitrogen stream.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

**EXAMPLE 4****Ethylene/1-butene copolymerization in gas phase**

Into a 1.35 litre steel autoclave, provided with stirrer, manometer, temperature indicator, supplying system for the catalyst, feeding lines of the monomers and thermostating jacket, purified by washing with ethylene at 70 °C, 60 g of NaCl, previously dried were introduced at room temperature. Thereafter, the amounts of ethylene, 1-butene and hy-

drogen reported in Table 3 were supplied. The suspension of the catalyst was prepared as follows. Into a dropping funnel the solid catalyst of example 2(A) and a solution of aluminium triisobutyl in 10 ml of hexane (TIBAL) was introduced. After 5 minutes, at the temperature of 20 °C, the suspension was injected into the autoclave, thermostatted at 45 °C, by slight ethylene overpressure. The temperature was then brought in about 5 minutes to the value requested for the polymerization and kept constant for the duration of the polymerization. The total pressure was kept constant by feeding an ethylene/1-butene mixture. The reaction was then interrupted by quick degassing of the monomers and the polymer obtained was washed at room temperature with distilled water first and thereafter with acetone, then it was dried in oven at 60 °C under nitrogen stream.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### **EXAMPLE 5**

##### **Ethylene/1-butene copolymerization in gas phase**

It was worked according to the procedure described in example 4, but using 2.019 g of the pre-polymerized solid catalyst of example 2(B) without further addition of TIBAL.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### **EXAMPLE 6**

##### **(A) Preparation of a supported catalyst**

It was worked according to the procedure described in example 2(A), but 224.2 g of rac-ethylene-bis(4,7-dimethyl-indenyl)zirconium dichloride instead of ethylene-bis-(indenyl)zirconium dichloride were used. 7.9 g of a product showing microspheroidal morphology was obtained, having the following composition: Al= 9.6%, Cl= 0.70%, Zr= 0.44%.

#### **EXAMPLE 7**

##### **Ethylene homopolymerization**

Into a 4.25 litre steel autoclave, provided with agitator, manometer, temperature indicator, supplying system for the catalyst, feeding line of monomers and thermostating jacket, purified by washing with propane at 70 °C, 2.3 litres of propane and the amounts of ethylene and hydrogen indicated in Table 1 were introduced. The suspension of the catalyst was prepared as follows. Into a dropping funnel the solid catalyst of example 6 and a solution of aluminium triisobutyl in 10 ml of hexane (TIBAL) was introduced. After 5 minutes, at the temperature of 20 °C, the suspension was injected into the autoclave, thermostatted at 45 °C, by slight ethylene overpressure. The temperature was then brought over about 5 minutes to the value requested for the polymerization and maintained constant by feeding ethylene. Then the reaction was ceased by quick degassing of the monomers and the polymer obtained was dried in oven at 60 °C under nitrogen stream.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### **EXAMPLE 8**

##### **Ethylene/1-butene copolymerization**

It was worked according to the procedure described in example 3, but using a 4.25 litre autoclave into which 2.3 litres of propane and the amounts of 1-butene, ethylene and hydrogen indicated in Table 1 were introduced. The suspension of the catalyst, prepared as described in example 7, was injected into the autoclave, thermostatted at 45 °C, by slight ethylene overpressure.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

**EXAMPLE 9**Preparation of a functionalized polystyrenic support**(A) Acylation**

Into a 6 litre reactor equipped with a mechanical stirrer and a thermostating system, 4300 ml of methylene chloride and 225 g of the polystyrenic resin prepared in example 1 were introduced. This was cooled to 10°C and 580 g of previously ground  $\text{AlCl}_3$  were rapidly added. Whilst maintaining the temperature at 10°C, 230 ml of acetyl chloride were added drop-wise over 1 hour. The reaction mixture was kept stirred at 25°C for a further 24 hours. The reaction mixture was cautiously poured into a suspension consisting of 2160 ml of distilled water, 2160 g of water and 2160 ml of 37% HCl solution. Once the addition was completed, it was left whilst stirring for a further 15 minutes, then the solid residue was filtered and repeatedly washed with distilled water and then acetone and then methanol. The product obtained was dried at 60°C; 260 g of product was obtained. The IR spectra showed a band centred at  $1680\text{ cm}^{-1}$  relating to the carbonyl group.

**(B) Reduction**

In a 3 litre round bottomed flask equipped with a mechanical stirrer and a thermostating system, 1060 ml of methanol and 260 g of the acylated resin prepared at point (A) was introduced. Whilst maintaining the temperature of the suspension below 35°C, a solution consisting of 138 g of  $\text{NaBH}_4$ , 170 ml of 20% NaOH and 1060 ml of distilled water was added over 2 hours. This was left to react for 48 hours at 25°C and then 200 ml of acetone was slowly added to destroy the excess  $\text{NaBH}_4$ . The resin was then filtered and repeatedly sequentially washed with distilled water, acetone, methanol and acetone. This was then dried under vacuo at 60°C for 24 hours. 234 g of product was obtained. The IR analysis showed an enlarged band centred at  $3440\text{ cm}^{-1}$ , whilst the carbonyl band at 1680 had disappeared. The content of hydroxyl groups, determined by gas-volumetric titration with aluminium triethyl, is of 1.9 meq per gram of resin. The spherical shaped particles showed an average size of  $150\text{ }\mu\text{m}$  with the following surface area and porosity characteristics:  $327\text{ m}^2/\text{g}$  and  $0.7\text{ ml/g}$  with average pore diameter of  $43\text{ }\text{\AA}$  (B.E.T.), and  $144\text{ m}^2/\text{g}$  and  $1.53\text{ ml/g}$  with pores of  $212\text{ }\text{\AA}$  (Hg).

**EXAMPLE 10**(A) Preparation of a supported catalyst

100 ml of toluene and 5.45 g of the support prepared in example 9(B) were introduced into a 350 ml jacketed reactor equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. The suspension was thermostatted at -5°C and 30 ml of a 1.04M solution of MAO (156 mg Al/g support) was added over 40 minutes. This was kept at -5°C for 1 hour then heated to 30°C and kept at this temperature for 1 hour and finally heated to 80°C for 4 hours. The whitish suspension obtained was once again cooled to -10°C and a solution of 50 ml of toluene and 246.1 mg of  $\text{EBIZrCl}_2$  (9.2 mg Zr/g support) was added over 40 minutes. The orange coloured solution was subsequently heated to 0°C and kept stirred for 30 minutes and then a further 2 hours at 30°C. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 9.0 g of spherical particles was recovered, having the following composition: Zr= 0.55%, Cl=1.38%, Al=9.5%.

**(B) Pre-polymerization**

It was worked according to the procedure described in example 2(B), but using 1.33 g of the supported catalyst prepared at point (A) of this example and continuing ethylene feeding for 5 hours. 6.1 g of pre-polymer was obtained.

**EXAMPLE 11**Ethylene/1-butene copolymerization

A 2.5 l steel autoclave equipped with a blade magnetic stirrer, manometer, temperature indicator, system for loading the catalyst, feed line for the monomer and a thermostating jacket, was purged through propane washing at 70°C. 5 mmols of TIBAL in 5 ml of hexane, 1260 ml of propane and the amounts of ethylene, propylene and hydrogen reported in Table 1 were introduced at room temperature and then the reactor was heated to 45°C. The catalytic suspension

was prepared in a Schlenck tube with a discharge tap at the bottom. 5 mmols of TIBAL in 5 ml of hexane was added at a temperature of 25°C and followed by 108 mg of supported catalyst from example 10(A). The reagents were contacted for 5 minutes and then the suspension was introduced into the autoclave by ethylene overpressure. The temperature was then raised to 50°C and maintained constant by feeding a mixture of ethylene/1-butene in a molar ratio of 18. The polymerisation was interrupted by introducing 0.6 NL of CO into the autoclave after rapid cooling to 30°C. The reactor was then left to slowly degas and the polymer obtained was dried at 60°C under vacuo.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### EXAMPLE 12

##### Ethylene homopolymerization

A 1.35 l steel autoclave equipped with a blade magnetic stirrer, manometer, temperature indicator, system for loading the catalyst, feed line for the monomer and a thermostating jacket, was purged through ethylene washing at 70°C. At room temperature 5 mmols of TIBAL in 700 ml of hexane, the amount of ethylene reported in Table 1 was introduced and then the reactor was heated to 75°C. The catalytic suspension was prepared in a Schlenck tube with a discharge tap at the bottom. 5 mmols of TIBAL in 5 ml of hexane was added at a temperature of 25°C and followed by 390 mg of supported catalyst from example 10(A). The reagents were contacted for 5 minutes and then the suspension was introduced into the autoclave by ethylene overpressure. The temperature was then raised to 50°C and maintained constant by feeding ethylene. The polymerisation was interrupted by introducing 0.6 NL of CO into the autoclave after rapid cooling to 30°C. The polymeric suspension was filtered and the polymer obtained was dried at 60°C under vacuo.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### EXAMPLE 13

##### Propylene homopolymerization

A 4.25 l steel autoclave equipped with a blade magnetic stirrer, manometer, temperature indicator, system for loading the catalyst, feed line for the monomer and a thermostating jacket, was purged through propylene washing at 70°C. At 40°C in a light flow of propylene, 10 mmols of TIBAL in 10 ml of hexane and 204 mg of catalyst of example 10(A) were introduced. 4250 ml of propylene were then added and the temperature was raised to 50°C. The pressure was maintained constant by feeding propylene. After two hours the reactor was left to degas and the recuperated polymer was dried at 60°C under vacuo. 18 g of polypropylene granules were obtained having the following characteristics:

T.B.D.	0.40 g/ml
intrinsic viscosity	0.40 dl/g
DSC melting peak (II scanning)	134°C
heat of fusion ( $\Delta H$ )	79 J/g
xylene insolubles at 25°C	91.2%
GPC Mw	34900 g/mol
Mw/Mn	2.2

#### EXAMPLE 14

##### Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 11, but using 570 mg of the pre-polymerized catalyst of example 10(B) instead of the supported catalyst.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

**EXAMPLE 15**Preparation of a supported catalyst

Into a 350 ml jacketed reactor equipped with a blade magnetic stirrer, thermometer, reflux condenser and a thermoregulator system, 100 ml of toluene and 5.47 g of the support prepared in example 9(B) were introduced. The suspension was thermostatted at -10°C and a solution, prereacted for 30 minutes at room temperature, consisting of 40 ml of toluene containing 1.85 g of MAO (157 mg Al/g support) and 243.4 mg of  $\text{EBIZrCl}_2$  (9.7 mg Zr/g support) were added over 40 minutes. The orange coloured suspension was subsequently heated to 0°C over 1 hour and kept stirred for 30 minutes and then 35°C for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 10.8 g of spheroidal particles was recovered, having the following composition: Zr= 0.48%, Al= 7.7%, solvent= 13.7%.

**EXAMPLE 16**Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 11, but using 121 mg of the supported catalyst prepared in example 15.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

**EXAMPLE 17**Preparation of a supported catalyst

Into a 350 ml jacketed reactor equipped with a blade magnetic stirrer, thermometer, reflux condenser and a thermoregulator system, 100 ml of toluene and 5.6 g of the support prepared in example 9(B) were introduced. The suspension was thermostatted at -10°C and 20 ml of a 0.83 M MAO solution were added over 30 minutes. This was kept at -10°C for 30 minutes then heated to 30°C and kept at this temperature for 1 hour. The whitish suspension obtained was once again cooled to 0°C and a prereacted solution consisting of 30 ml of toluene and 261.4 mg of  $\text{EBIZrCl}_2$  (9.2 mg Zr/g support) and 0.88 mg of MAO, was added over 40 minutes. The orange coloured solution was kept stirred for 1 hour at 0°C. Slowly (over 2 hours) the suspension was heated to 30°C and maintained at this temperature for 1 hour. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 5.6 g of spheroidal particles was recovered, having the following composition: Zr= 0.64%, Cl= 1.25%, Al= 9.0%.

**EXAMPLE 18**Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 11, but using 165 mg of the supported catalyst prepared in example 17.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

**EXAMPLE 19**Preparation of a supported catalyst

100 ml of toluene and 10.15 g of the support prepared in example 9(B) were introduced into a 350 ml jacketed reactor equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. The suspension was thermostatted at -10°C and 50 ml of a 1.16 M solution of MAO (154 mg Al/g support) was added over 50 minutes. This was kept at -10°C for 1 hour then heated to 0°C and kept at this temperature for 1 hour, at 30°C for 1 hour and finally heated to 80°C for 4 hours. The whitish suspension obtained was left to decant, the liquid separated and the solid support was subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. After drying 13.8 g of spherical particles was recovered, having the following com-

position: Al=8.95%, solvent=7.6%.

Using the same apparatus, 5.6 g of the resin treated with MAO were dispersed in 100 ml of anhydrous toluene and cooled to 0°C. A solution consisting of 50 ml of toluene and 228 mg of EBDMIZrCl<sub>2</sub> (7.8 mg Zr/g support) were added over 1 hour. The purply-red coloured solution was left at 0°C for 1 hour and subsequently heated to 30°C and kept stirred for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 5.4 g of spheroidal particles was recovered, having the following composition: Zr= 0.44%, Cl= 1.09%, Al= 8.1%.

#### EXAMPLE 20

##### Ethylene/1-hexene copolymerization

A 2.5 l steel autoclave equipped with a blade magnetic stirrer, manometer, temperature indicator, system for loading the catalyst, feed line for the monomer and a thermostating jacket, was purged through propane washing at 70°C. 5 mmols of TIBAL in 5 ml of hexane, 1260 ml of propane, 277 ml of 1-hexene and the amounts of ethylene and hydrogen reported in Table 1 were introduced at room temperature and then the reactor was heated to 55°C. The catalytic suspension was prepared in a Schlenck tube with a discharge tap at the bottom. 5 mmols of TIBAL in 5 ml of hexane was added at a temperature of 25°C and followed by 150 mg of the supported catalyst prepared in example 19. The reagents were contacted for 5 minutes and then the suspension was introduced into the autoclave by ethylene overpressure. The temperature was then raised to 60°C and maintained constant during the polymerisation. The total pressure was kept constant by feeding ethylene. The polymerisation was interrupted by introducing 0.6 NL of CO into the autoclave after rapid cooling to 30°C. The reactor was then left to slowly degas and the polymer obtained was dried at 60°C under vacuo.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### EXAMPLE 21

##### Preparation of a supported catalyst

300 ml of toluene and 30.2 g of the support prepared in example 9(B) were introduced into a 750 ml jacketed reactor equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. The suspension was thermostatted at -10°C and 200 ml of a 0.9 M solution of MAO (160 mg Al/g support) was added over 70 minutes. This was kept at -10°C for 1 hour then heated to 0°C and kept at this temperature for 1 hour, at 30°C for 1 hour and finally heated to 80°C for 4 hours. The whitish suspension obtained was left to decant, the liquid separated and the solid was subjected to two washings with 200 ml of toluene and one with 200 ml of anhydrous hexane. After drying 66 g of spheroidal particles were recovered: having the following composition: Al= 7.5%, solvent= 27%.

Using the same apparatus, 10.6 g of the resin treated with MAO were dispersed in 300 ml of anhydrous toluene and cooled to 0°C. A solution consisting of 50 ml of toluene and 176.8 mg of EBTHIZrCl<sub>2</sub> (7.7 mg Zr/g support) were added over 1 hour. The solution was left at 0°C for 30 minutes and subsequently heated to 30°C and kept stirred for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 8.7 g of spheroidal particles was recovered, having the following composition: Zr= 0.40%, Cl= 0.92%, Al= 7.8%.

#### EXAMPLE 22

##### Ethylene/propylene copolymerization

Into a 4.25 litre steel autoclave, provided with agitator, manometer, temperature indicator, supplying system for the catalyst, feeding lines of the monomers and thermostating jacket, purified by washing with propylene at 70°C, 2 litres of propylene and the ethylene amounts indicated in Table 3 were introduced at room temperature. The suspension of the catalyst was prepared as described in example 4, but using 220 mg of the supported catalyst prepared in example 21, and injected into the autoclave at room temperature by a steel vial and under propylene pressure. The temperature was then brought in about 5 minutes to the value requested for the polymerization and kept constant for the polymerization time. The pressure was maintained constant by feeding ethylene. Thereafter, the reaction was interrupted by a quick degassing of the monomers and the polymer obtained was dried in oven at 60 °C under nitrogen stream.

The polymerization conditions and the data relating to the characterization of the obtained polymer are reported in Table.3.



**EXAMPLE 23**Ethylene/propylene copolymerization

It was worked according to the procedure described in example 22, but using 20 mg of the supported catalyst of example 21.

The polymerization conditions and the data relating to the characterization of the obtained polymer are reported in Table 3.

**EXAMPLE 24**Preparation of a functionalized polystyrenic support(A) Chloromethylation

In a 500 ml 3-neck flask supplied with mechanical stirrer and water refrigerator were placed 30 g of cross-linked polystyrene having the following characteristics:

Average particle size	248 $\mu\text{m}$
Surface area (B.E.T.)	891 $\text{m}^2/\text{g}$
(Hg)	112 $\text{m}^2/\text{g}$
Porosity (B.E.T.)	2.21 $\text{ml/g}$
(Hg)	1.32 $\text{ml/g}$

17.25 g of trioxane, 8.6 g of  $\text{ZnCl}_2$ , 250 ml of 37% aqueous HCl and 50 ml of dioxane. A rapid stream of HCl gas was poured through the reaction mixture and it was kept out at 80°C for 4 hour and at 100°C for 3 hours. Then, the suspension was cooled to room temperature and washed several time with water and  $\text{Na}_2\text{CO}_3$  water solution. Part of the solid compound was dried under vacuum at 60°C and the chlorine content was detected resulting 6.1 wt. %.

(B) Hydrolysis

The remaining part of the wet polymer, 40 g of  $\text{Na}_2\text{CO}_3$ , 360 ml of dioxane and 240 ml of distilled water were placed in a 1 l autoclave. The autoclave was closed and the reaction was carried out at 160-162°C, reaching a pressure of 7.5-8 bar. after 5 hours, the polymer was filtered at room temperature and washed many times with water, than with a mixture 1-1 water-acetone, than with acetone and finally with methanol. After drying under vacuum at 60°C, 32 g of polymer were recovered. The following characteristics were found:

Chlorine content	1.6 wt%
Functional groups	1.22 meq/g
Average particle size	240 $\mu\text{m}$
Surface area (B.E.T.)	621 $\text{m}^2/\text{g}$
(Hg)	118 $\text{m}^2/\text{g}$
Porosity (B.E.T.)	1.34 $\text{ml/g}$
(Hg)	1.18 $\text{ml/g}$
IR analysis	broad peak centered at 2400 $\text{cm}^{-1}$ (OH)

**EXAMPLE 25**Preparation of a supported catalyst

100 ml of toluene and 5.5 g of the support prepared in example 24(B) were introduced into a 350 ml jacketed reactor equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. The suspension was thermostatted at -10°C and 50 ml of a 0.61 M solution of MAO (151 mg Al/g support) was added over 60 minutes. This was kept at -10°C for 1 hour then heated to 0°C and kept at this temperature for 1 hour, at 30°C for 1 hour and finally heated to 80°C for 3 hours. The whitish suspension obtained was left to decant, the liquid separated and the solid support was subjected to two washings with 100 ml of toluene and then dispersed once again in 150 ml of anhy-

drous toluene. After cooling to 0°C, a solution consisting of 50 ml of toluene and 230 mg of  $\text{EBIZrCl}_2$  (9.1 mg Zr/ g support) were added over 1 hour. The reddish coloured solution was left at 0°C for 1 hour and subsequently heated to 30°C and kept stirred for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 6.4 g of spheroidal particles was recovered, having the following composition: Zr= 0.54%, Cl= 1.48%, Al= 5.82%.

#### EXAMPLE 26

##### Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 11, but using 538 mg of the supported catalyst prepared in example 25.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### EXAMPLE 27

##### Preparation of a functionalized polystyrenic support

##### (A) Tert-butylated polystyrene

Into a 2 litre glass reactor, equipped with thermometer, reflux condenser, blade stirrer and thermoregulation system, an aqueous solution consisting of:

- 400 ml of distilled water
- 36.2 ml of a ROAGIT SVM (Rhom) 5 wt.% solution in water
- 2.25 g of PROLIT C10 (Caffaro)
- 0.45 g of sodium chloride

was introduced under nitrogen atmosphere. The whole was stirred at 400 rpm at room temperature for 1 hour. Thereafter an organic solution consisting of:

- 225 ml of n-octane
- 75 ml of toluene
- 120 ml of 55 wt% of divinylbenzene in ethylvinylbenzene
- 45 ml of p-tert-butoxystyrene (Hokko Chemical Industry)
- 3.13 g of 75 wt% dibenzoylperoxide in water

was introduced.

The temperature of the reactor was raised to 80°C over 1 hour, kept for 8 hours, then cooled to 50°C and 700 ml of distilled water were added. The solid product was separated by filtration and subjected to repeated washings with distilled water, extraction with methanol at 50°C and, subsequently, drying at 100°C and 1 mmHg of residual pressure. 108 g of product showing microspheroidal morphology was obtained. The product has the following characteristics:

Surface area (B.E.T.)	411 m <sup>2</sup> /g
(Hg)	86 m <sup>2</sup> /g
Porosity (B.E.T.)	0.85 ml/g
(Hg)	0.66 ml/g
Average radius pore	41 Å
Average particle size	170 µm
IR analysis	peak at 1240 cm <sup>-1</sup> (Aryl-O-t-Bu)

##### (B) Hydrolysis

Into a 500 ml glass reactor, provided with thermometer, reflux condenser, blade stirrer and thermoregulation system, 200 ml of hydrochloric acid (37 % solution) and 36.5 g of the support prepared at point (A) of this example were introduced. The mixture was thermostatted at 90°C and kept stirred for 8 hours. The solid was separated and added

of 200 ml of freshly HCl and kept at 90°C for a further 4 hours. After filtration, the recovered solid was washed with water till a pH=7 of the washing, then washed with acetone and dried under vacuum at 60°C. 34.7 g of spherical particle were recovered, having 1.5 meq/g of functional groups. The IR analysis shows a sharp peak at 3450 cm<sup>-1</sup> and the peak at 1240 cm<sup>-1</sup> disappears.

#### EXAMPLE 28

##### Preparation of a supported catalyst

100 ml of toluene and 5.3 g of the polystyrenic support prepared in example 27(B) were introduced into a 350 ml jacketed reactor equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. The suspension was thermostatted at 0°C and 33 ml of a toluene solution containing 5 g of triethyl aluminium. Once the addition was completed, the solution was heated to 25°C and kept stirred for 1 hour. After filtering the liquid phase, the solid was washed in toluene and once again dispersed in 100 ml toluene. The suspension was then thermostatted at -5°C and 25 ml of a 1.37 M solution of MAO (176 mg Al/g support) was added over 20 minutes. This was heated to 0°C and kept at this temperature for 1 hour, at 30°C for 1 hour and finally heated to 80°C for 4 hours. After cooling to -10°C, 50 ml of toluene and 218 mg of EBI<sub>2</sub>ZrCl<sub>2</sub> (9.0 mg Zr/g support) was added over 1 hour. The reddish coloured solution was left at 0°C for 1 hour and subsequently heated to 30°C and kept stirred for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 6.0 g of spheroidal particles was recovered, having the following composition: Zr= 0.42%, Cl= 1.1%, Al= 11.9%.

#### EXAMPLE 29

##### Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 11 but using 185 mg of the supported catalyst prepared in example 28.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### EXAMPLE 30

##### Preparation of a functionalized polystyrenic support

100 ml of cyclohexane, 13.8 g of the polystyrenic resin prepared in example 1, and 17.8 ml of N,N,N',N'-tetramethyl ethylene diamine (TMEDA) were introduced into a 350 ml jacketed reactor maintained in an inert atmosphere (N<sub>2</sub>), equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. Maintaining the temperature of the suspension at 20-22°C, 100 ml of a solution of 1.6 M n-butyl lithium was fed over 1.5 hours. The suspension changed from yellow through orange and finally red. This was then heated to 65°C and kept at this temperature for 4.5 hours. The solid was then filtered, whilst keeping under an inert atmosphere, and subjected to two washings with 100 ml of cyclohexane and then 150 ml of tetrahydrofuran (THF) was added previously saturated with CO<sub>2</sub>. Then about 300 g of solid CO<sub>2</sub> was directly added to the suspension whilst stirring continuously. The colour of the solution became whitish. The suspension was left to react overnight, then filtered and the solid was subjected to repeated washings with a solution THF/HCl, methanol/HCl, methanol and then finally dried under vacuo at 40°C. 14 g of spherical resin was obtained having the following characteristics:

Functional groups	1.2 meq/g
Average radius pore	37 Å
Average particle size	150 µm
Surface area (B.E.T.)	303 m <sup>2</sup> /g
(Hg)	129 m <sup>2</sup> /g
Porosity (B.E.T.)	1.12 ml/g
(Hg)	1.69 ml/g
IR analysis	peak at 1700 cm <sup>-1</sup> (-C=O)
	peak at 3400 cm <sup>-1</sup> (-OH)

**EXAMPLE 31**Preparation of a supported catalyst

100 ml of toluene and 5.7 g of the support from example 30 were introduced into a 350 ml jacketed reactor equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. The suspension was thermostatted at 0°C and 10 ml of a toluene solution containing 1.5 g of triethyl aluminium. Once the addition was completed, the solution was heated to 80°C and kept stirred for 1 hour. After filtering the liquid phase, the solid was washed in toluene and once again dispersed in 100 ml toluene. The suspension was then thermostatted at 0°C and 50 ml of a 0.64 M solution of MAO (153 mg Al/g support) was added over 40 minutes. This was kept at 0°C for 1 hour, heated to 30°C for 1 hour and finally 80°C for 4 hours. After cooling to room temperature, the suspension was filtered and once again 100 ml of anhydrous toluene was added. The suspension was cooled to 0°C and a solution consisting of 40 ml of toluene and 212 mg of  $\text{EBIZrCl}_2$  (8.1 mg Zr/g support) was added. The reddish coloured solution was heated to 30°C and kept stirred for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at 25°C. 5.9 g of spheroidal particles was recovered, having the following composition: Zr= 0.2%, Cl= 0.46%, Al= 7.2%.

**EXAMPLE 32**Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 3 but using 370 mg of the supported catalyst prepared in example 31.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

**EXAMPLE 33**Preparation of a functionalized polystyrenic support(A) Methylated polystyrene

Into a 2 litre glass reactor, equipped with thermometer, reflux condenser, blade stirrer and thermoregulation system, an aqueous solution consisting of:

- 400 ml of distilled water
- 30 ml of a ROAGIT SVM (Rhom) 5 wt. % solution in water
- 2.25 g of PROLIT C10 (Caffaro)
- 0.45 g of sodium chloride

was introduced under nitrogen atmosphere. The whole was stirred at 400 rpm at room temperature for 1 hour. Thereafter an organic solution consisting of:

- 225 ml of n-octane
- 75 ml of toluene
- 120 ml of 55 wt% of divinylbenzene in ethylvinylbenzene
- 31.5 ml of m and p-methylstyrene
- 3.13 g of 75 wt% dibenzoylperoxide in water

was introduced.

The temperature of the reactor was raised to 80°C over 1 hour, kept at this temperature for 9 hours, then cooled to 50°C and 700 ml of distilled water was added. The solid product was separated by filtration and subjected to repeated washings with distilled water, HCl (5 wt%) solution, distilled water and extraction with methanol at 50°C. Subsequently, the solid was dried at 100°C and 1 mmHg of residual pressure.

117 g of product showing microspheroidal morphology was obtained. The product has the following characteristics:

Average radius pore	69 Å
---------------------	------

(continued)

Average particle size	150 $\mu\text{m}$
Surface area (B.E.T.)	495 $\text{m}^2/\text{g}$
(Hg)	137 $\text{m}^2/\text{g}$
Porosity (B.E.T.)	1.72 $\text{ml/g}$
(Hg)	1.87 $\text{ml/g}$

(B) Acetylation

Into a 1500 ml glass reactor, provided with thermometer, reflux condenser, blade stirrer and thermoregulation system, 1000 ml of acetic acid and 20 g of the support prepared at point (A) of this example were introduced. Slowly 56 g of  $\text{Mn}(\text{OAc})_3 \cdot 3\text{H}_2\text{O}$  were added. Maintaining the temperature below  $40^\circ\text{C}$ , 100 ml of sulphuric acid (96 %) were dropped into the stirred suspension. The mixture was then thermostatted at  $45^\circ\text{C}$  and kept stirred for 4 hours. After filtration, the recovered solid was washed with a  $\text{NaHCO}_3$  solution, water, methyl alcohol, finally with acetone and dried under vacuo at  $80^\circ\text{C}$  for 5 hours. 23 g of spherical particle- were recovered. The IR analysis show a peak at  $1740\text{ cm}^{-1}$  ( $-\text{C}=\text{O}$ ) and a peak at  $1220\text{ cm}^{-1}$  ( $-\text{OAc}$ ).

(C) Hydrolysis

Into a 1 l glass reactor, provided with thermometer, reflux condenser, blade stirrer and thermoregulation system, 500 ml of toluene, 200 ml of 40 wt % KOH solution, the product prepared at point (B) of this example and 10 ml of 40 wt%  $\text{Bu}_4\text{NOH}$  solution in water, were introduced. The mixture was thermostatted at  $85^\circ\text{C}$  and kept stirred for 21 hours. The solid was separated and washed with 300 ml of a HCl/water solution, then washed with distilled water, methyl alcohol, acetone and dried under vacuo at  $80^\circ\text{C}$ . 19 g of spherical particle were recovered.

The IR analysis showed a broad peak at  $3400\text{ cm}^{-1}$  and the peaks at  $1740$  and  $1220\text{ cm}^{-1}$  had totally disappeared. The titration with aluminium triethyl indicated 1.5 meq/g of  $-\text{OH}$  group.

**EXAMPLE 34**Preparation of a supported catalyst

100 ml of toluene and 3.9 g of the support prepared in example 33(C) were introduced into a 350 ml jacketed reactor equipped with a blade stirrer, thermometer, reflux condenser and a thermoregulator system. The suspension was thermostatted at  $-10^\circ\text{C}$  and 50 ml of a 0.51 M solution of MAO (178 mg Al/g support) was added over 20 minutes. This was kept at  $-10^\circ\text{C}$  for 1 hour whilst stirring, heated to  $0^\circ\text{C}$  for 1 hour,  $30^\circ\text{C}$  for 1 hour and finally  $80^\circ\text{C}$  for 4 hours. The suspension was filtered, washed with 100 ml of toluene and once again 100 ml of anhydrous toluene was added. After cooling to  $0^\circ\text{C}$ , a solution consisting of 50 ml of toluene and 194 mg of  $\text{EBIZrCl}_2$  was added over 1 hour. The reddish coloured solution was left at  $0^\circ\text{C}$  for 1 hour and then subsequently heated to  $30^\circ\text{C}$  and kept stirred for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous hexane and finally dried under vacuo at  $25^\circ\text{C}$ . 6.5 g of spheroidal particles was recovered, having the following composition: Zr= 0.55%, Cl= 1.1%, Al= 10.2%.

**EXAMPLE 35**Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 11 but using 1085 mg of the supported catalyst prepared in example 34.

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

**EXAMPLE 36 (comparison)**Preparation of a supported catalyst

100 ml of anhydrous toluene and 5.15 g of the polystyrenic resin prepared in example 1 were introduced into a

350 ml glass reactor, provided with thermometer, reflux condenser, blade stirrer and thermoregulation system. The mixture, thermostatted at 0 °C and kept under stirring, was added with 40 ml of a 0.74 M toluene solution of methylalumoxane (MAO). This was reacted at a temperature of 0 °C for 1 hour, then at a temperature of 30 °C for 1 hour, then at a temperature of 80 °C for 4 hours. After having cooled to 25 °C, 50 ml of a toluene solution containing 196.7 mg of ethylene-bis(indenyl)zirconium dichloride were added within 30 minutes. The temperature was raised to 30 °C whilst keeping stirred for 2 hours. A reddish solution was obtained; this was allowed to decant, thus obtaining a precipitate and a yellowish solution which was removed by drainage. The precipitate was repeatedly washed with anhydrous toluene and thereafter dried under vacuum. 6 g of product showing microspheroidal morphology were obtained, having the following composition: Zr= 0.26%, Cl=0.2%, Al=6.2%.

#### **EXAMPLE 37 (comparison)**

##### Ethylene/1-butene copolymerization

It was worked according to the procedure described in example 8, but using 478 mg of the supported catalyst prepared in example 36 (comparison).

The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

#### **EXAMPLE 38 (comparison)**

##### Preparation of a functionalized polystyrenic support

285 ml of methylene chloride and 16 g of a polystyrenic resin (Fluka product 4% DVB) were introduced into a 750 ml reactor equipped with a mechanical stirrer and a thermostating system. This was cooled to 10°C and 41 g of aluminium trichloride in finely divided powder form were rapidly added. Maintaining the internal reactor temperature at 10°C, 15.5 ml of acetyl chloride were added dropwise over 20 minutes. the reaction mixture was kept stirred at 25°C for a further 24 hours and then cautiously poured into a suspension consisting of 150 ml of hydrochloric acid (37%) and 200 g of crushed ice. Once the addition was completed it was left whilst stirring for a further 30 minutes and, after filtration, the solid was repeatedly washed with distilled water, methanol, and acetone. The obtained product was then dried at 60°C under vacuo. The solid product previously obtained was introduced, together with 75 ml of methanol, into a 750 ml reactor equipped with a mechanical stirrer and a thermostating system. After thermostating at 30°C, a solution consisting of 9.2 g of NaBH<sub>4</sub>, 11.5 ml of NaOH (20%) and 70 ml of distilled water was added. This was left to react at 35°C for 72 hours, then slowly 100 ml of acetone was added to destroy the excess NaBH<sub>4</sub>. The resin was then filtered and repeatedly washed with distilled water, acetone, methanol and acetone. This was then dried for 4 hours at 40°C. 19 g of spherical product was obtained, having the following characteristics:

Functional groups                      0.2 meq/g

Surface area      (B.E.T.)      non detectable

		(Hg)	0.14 m <sup>2</sup> /g
5	Porosity	(B.E.T.)	non detectable
		(Hg)	0.01 ml/g
10	Average particle size		110 μm
	IR analysis		peak at 1701 cm <sup>-1</sup> (-C=O)
15			broad peak at 3400 cm <sup>-1</sup> (-OH)

**EXAMPLE 39 (comparison)**Preparation of a supported catalyst

20 Into a 350 ml jacketed reactor equipped with a blade magnetic stirrer, thermometer, reflux condenser and a thermoregulator system, 100 ml of toluene and 5.6 g of the polystyrenic support prepared in example 38 (comparison) were introduced. The suspension was thermostatted at -10°C and 50 ml of 0.68 solution of MAO (166 mg Al/g support) were added over 60 minutes. This was kept at -10°C for 1 hour, heated to 0°C for 1 hour, 30°C for 1 hour and finally  
 25 80°C for 3 hours. The suspension obtained was left to decant, the liquid separated and the solid subjected to two washings with 100 ml of toluene and once again dispersed in 100 ml of anhydrous toluene. After cooling to 0°C, a solution consisting of 50 ml of toluene and 221 mg of EBI<sub>2</sub>ZrCl<sub>2</sub> was added over 1 hour. The reddish coloured solution was left at 0°C for 1 hour and then subsequently heated to 30°C and kept stirred for 2 hours. After decanting the solid, the liquid was filtered and the residue subjected to two washings with 100 ml of toluene and one with 100 ml of anhydrous  
 30 hexane and finally dried under vacuo at 25°C. 5.0 g of spheroidal particles was recovered, having the following composition: Zr= 0.09%, Cl= 0.08%, Al= 1.69%.

**EXAMPLE 40 (comparison)**Ethylene/1-butene copolymerization

35 It was worked according to the procedure described in example 11, but using 1460 mg of the supported catalyst prepared in example 39 (comparison).

40 The polymerization conditions are reported in Table 1. The data relating to the characterization of the obtained polymer are reported in Table 2.

Table I

Example	catalyst (mg)	TIBAL (mmol)	$\alpha$ -olefin type	ethylene partial pressure (bar)	hydrogen partial pressure (bar)	time (min)	temperature (°C)	Yield (g)	Activity (g/gcat)
3	160	5	1-butene	165	0.05	120	50	174	1088
4	323	5	1-butene	25.6	0.01	120	50	130	402
5	2019#	-	1-butene	25.6	0.01	60	50	72	204
7	235	10	-	8.12	0.04	60	50	111	472
8	157	10	1-butene	16.5	0.05	120	50	232	1474
11	108	10	1-butene	15.9	-	240	50	250	2300
12	390	10	-	9.6	-	120	80	110	281
16	121	10	1-butene	15.9	-	240	50	157	1293



Example	catalyst (mg)	TIBAL (mmol)	$\alpha$ -olefin	ethylene partial pressure (bar)	hydrogen partial pressure (bar)	time (min)	temperature (°C)	Yield (g)	Activity (g/gcat)
18	165	10	1-butene	15.9	-	240	50	155	939
20	150	10	1-hexene	14.4	0.19	120	60	386	2563
26	538	10	1-butene	15.9	-	240	50	274	509
29	185	10	1-butene	15.9	-	240	50	204	1102
32	370	10	1-butene	16.5	0.05	120	50	102	273
35	1085	15	1-butene	15.9	-	240	50	96	88
37 (comp.)	478	10	1-butene	16.5	0.05	60	50	389	814
40 (comp.)	1460	10	1-butene	15.9	-	240	50	15	10

a) mol % of the 1-butene in the gas phase.  
 b) pre-polymerized catalyst

Table 2

Example	$\alpha$ -olefin (wt. %)	I.V. (dl/g)	absolute density (g/ml)	T <sub>m</sub> (°C)	DSC $\Delta H$ (J/g)	Tamped BD (g/ml)	Poured BD (g/ml)	Remarks
3	17	0.86	0.8985	88	68	0.45	0.41	granules
4	16	1.11	0.9100	72	69	0.38	0.35	"
5	6.3	1.35	0.9310	110	115	0.41	0.38	"
7	-	3.25	n.d.	134	166	0.44	0.39	"
8	13	1.92	0.9062	98	71	0.45	0.41	"
11	14.6	1.38	0.9030	87	70	0.43	0.39	spheres
12	-	2.26	-	133	186	0.33	0.28	"
16	14.8	1.37	0.9056	90	83	0.45	0.39	"

Example	$\alpha$ -olefin (wt. %)	I.V. (dl/g)	absolute density (g/ml)	DSC	Tamped BD (g/ml)	Poured BD (g/ml)	Remarks
18	14.5	0.86	0.9060	88	0.33	0.28	"
20	12.7*	2.37	0.9060	101	0.46	0.41	granules
26	11.9	1.65	0.9112	94	0.30	0.28	spheres
29	14.1	1.51	0.9043	91	0.36	0.33	granules
32	16	0.89	0.9110	86	0.53	0.48	spheres
35	13.2	1.12	0.9085	95	0.45	0.38	"
37 (comp.)	17.2	0.91	0.9024	92	0.24#	0.21#	15% powder, 85% agglomerate on the wall reactor
40 (comp.)	n.m.	2.11	n.m.	96	n.d	n.d	agglomerate

\*) 1-hexene comonomer  
 #) referred to the part in form of powder  
 n.m. - not measured  
 n.d. - non detectable

Table 3

Example	catalyst (mg)	TIBAL (mmol)	ethylene partial pressure (bar)	time (min)	temperature (°C)	Yield (g)	Activity (g/gcat)	propylene (wt. %)	T <sub>m</sub> (°C)	DSC  ΔH (J/g)	Remarks
24	221.4	10	12.6	60	50	806	3640	60	-	0	divided spheres
25	20.0	10	10.5	120	50	164	8200	44	-	0	"

## Claims

1. A supported catalyst for the polymerization of olefins, comprising:

- (A) a porous organic support functionalised with groups having active hydrogen atoms;  
 (B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur; and  
 (C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type.

2. The supported catalyst according to claim 1, wherein the organic support has a porosity higher than 0.2 cm<sup>3</sup>/g and a surface area higher than 30 m<sup>2</sup>/g.

3. The supported catalyst according to any of claims 1 or 2, wherein the organic support is in the form of particles having microspheroidal morphology with a diameter comprised between 5 and 1000 µm.

4. The supported catalyst according to any of claims 1 to 3, wherein the functional groups of the organic support are selected from hydroxy, primary amino, secondary amino, sulphonic, carboxylic, amido, N-monosubstituted amido, sulphonamido, N-monosubstituted sulphonamido, sulphhydryl, imido and hydrazido groups.

5. The supported catalyst according to any of claims 1 to 4, containing an amount of functional groups higher than 0.2 milliequivalent for each gram of solid support.

6. The supported catalyst according to any of claims 1 to 5, wherein the organic support is a partially cross-linked styrenic polymer.

7. The supported catalyst according to any of claims 1 to 6, wherein the transition metal compound is selected from cyclopentadienyl compounds of formula (I):



wherein M is Ti, Zr, Hf or V; C<sub>5</sub>R<sup>1</sup><sub>5-m</sub> and C<sub>5</sub>R<sup>1</sup><sub>5-m</sub> are cyclopentadienyl rings equally or differently substituted; substituents R<sup>1</sup>, same or different from each other, are hydrogen, alkyl, alkenyl, aryl, alkaryl or aralkyl radicals containing from 1 to 20 carbon atoms which can also contain Si or Ge atoms or Si(CH<sub>3</sub>)<sub>3</sub> groups, or also two or four substituents R<sup>1</sup> of a same cyclopentadienyl group can form one or two rings having from 4 to 6 carbon atoms; R<sup>2</sup> is a group which bridge links the two cyclopentadienyl rings and is selected from CR<sup>3</sup><sub>2</sub>, C<sub>2</sub>R<sup>3</sup><sub>4</sub>, SiR<sup>3</sup><sub>3</sub>, Si<sub>2</sub>R<sup>3</sup><sub>4</sub>, GeR<sup>3</sup><sub>2</sub>, Ge<sub>2</sub>R<sup>3</sup><sub>4</sub>, R<sup>3</sup><sub>2</sub>SiCR<sup>3</sup><sub>2</sub>, NR<sup>1</sup> or PR<sup>1</sup>, with substituents R<sup>3</sup>, same or different from each other, which are R<sup>1</sup> or two or four substituents R<sup>3</sup> can give one or two rings having from 3 to 6 carbon atoms; substituents Q, same or different from each other, are halogen, hydrogen, OH, SH, R<sup>1</sup>, OR<sup>1</sup>, SR<sup>1</sup>, NR<sup>1</sup><sub>2</sub> or PR<sup>1</sup><sub>2</sub>; m is 0 or 1; n is 0 or 1; being 1 when m=1; p is 2 or 3.

8. The supported catalyst according to any of claims 1 to 7, wherein the organo-metallic compound of aluminium is an alumoxane.

9. The supported catalyst according to any of claims 1 to 8, wherein the molar ratio between the organo-metallic compound of aluminium and the transition metal compound is comprised between 10 and 500.

10. A process for the preparation of a supported catalyst for the polymerization of olefins according to any of claims 1 to 9, comprising the steps of: contacting in an inert solvent

- (A) a porous organic support functionalised with groups having active hydrogen atoms, and  
 (B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur;

thereafter contacting the thus obtained product with

(C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type;

and finally recovering the supported catalyst by removing the solvent.

11. A process for the preparation of a supported catalyst for the polymerization of olefins according to any of claims 1 to 9, comprising the steps of: contacting in an inert solvent

(B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur, and

(C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type;

thereafter contacting the thus obtained product with

(A) a porous organic support functionalised with groups having active hydrogen atoms;

and finally recovering the supported catalyst by removing the solvent.

12. A process for the preparation of a supported catalyst for the polymerization of olefins according to any of claims 1 to 9, comprising the steps of: contacting in an inert solvent

(A) a porous organic support functionalised with groups having active hydrogen atoms, and

(B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur;

contacting in an inert solvent

(B) at least one organo-metallic compound of aluminium containing at least one heteroatom selected from oxygen, nitrogen and sulphur, and

(C) at least one compound of a transition metal selected from those of groups IVb, Vb or VIb of the Periodic Table of the Elements, containing at least one ligand of the cyclopentadienyl type;

thereafter contacting the product obtained by contacting (A) and (B) with the product obtained by contacting (B) and (C);

and finally recovering the supported catalyst by removing the solvent.

13. The process according to any of claims 10 to 12, wherein the organic support is pre-contacted with at least an aluminium alkyl compounds of formula (VI):



wherein  $R^5$  is selected among alkyl, alkenyl, aryl, alkaryl and aralkyl radicals containing from 1 to 10 carbon atoms, X is selected among hydrogen and halogen atoms, q is an integer comprised between 1 and 3.

14. The process according to claim 13, wherein the aluminium alkyl compound is triisobutylaluminium.

15. A supported and pre-polymerized catalyst for the polymerization of olefins obtainable by subjecting a supported catalyst according to any of claims 1 to 9 to a pre-polymerization treatment with at least one olefinic monomer.

16. A supported and pre-polymerized catalyst according to claim 15, wherein the amount of polymer produced is comprised between 0.5 and 10 parts by weight with respect to the weight of the supported catalyst.

17. The supported and pre-polymerized catalyst according to any of claims 15 or 16, comprising an alkyl aluminium compound of formula (VI):



wherein  $R^5$ , X and q are defined as above.

18. A process for the homo- or co-polymerization of olefins comprising the polymerization reaction of one or more olefinic monomers in the presence of a supported catalyst according to any of claims 1 to 9.
19. A process for the homo- or co-polymerization of olefins comprising the polymerization reaction of one or more olefinic monomers in the presence of a supported and pre-polymerized catalyst according to any of claims 15 to 17.
20. The process for the homo- or co-polymerization of olefins according to any of claims 18 or 19, wherein the catalyst is pre-contacted with at least one compound selected from the alkyl aluminium compounds of formula (VI):



wherein  $R^5$ , X and q are defined as above, and the organo-metallic compounds of aluminium containing at least one heteroatom selected from oxygen, nitrogen, sulphur.

21. The process for the homo- or co-polymerization of olefins according to claim 20, wherein the organo-metallic compound of aluminium are alumoxanes.

## Patentansprüche

1. Trägerkatalysator zur Polymerisation von Olefinen, umfassend

(A) einen porösen, organischen Träger, der funktionalisiert ist mit aktive Wasserstoffatome aufweisenden Gruppen;

(B) zumindest eine organo-metallische Verbindung des Aluminiums mit zumindest einem Heteroatom, ausgewählt unter Sauerstoff, Stickstoff und Schwefel;

(C) zumindest eine Verbindung eines Übergangsmetalls, ausgewählt unter denjenigen der Gruppen IVb, Vb oder VIb des Periodensystems der Elemente, die zumindest einen Liganden vom Cyclopentadienyl-Typ enthält.

2. Trägerkatalysator gemäß Anspruch 1, worin der organische Träger eine Porosität von höher als 0,2 cm<sup>3</sup>/g und eine spezifische Oberfläche von höher als 30 m<sup>2</sup>/g besitzt.

3. Trägerkatalysator gemäß einem der Ansprüche 1 oder 2, worin der organische Träger in Form von Teilchen mit mikrosphäroidischer Morphologie mit einem Durchmesser zwischen 5 und 1000 µm vorliegt.

4. Trägerkatalysator gemäß einem der Ansprüche 1 bis 3, worin die funktionellen Gruppen des organischen Trägers ausgewählt sind unter Hydroxy-, primären Amino-, sekundären Amino-, Sulfon-, Carboxyl-, Amido-, N-monosubstituierten Amido-, Sulfonamido-, N-monosubstituierten Sulfonamido-, Sulfhydryl-, Imido- und Hydrazidogruppen.

5. Trägerkatalysator gemäß einem der Ansprüche 1 bis 4, enthaltend eine Menge an funktionellen Gruppen von höher als 0,2 Milliäquivalent je Gramm Trägerkatalysator.

6. Trägerkatalysator gemäß einem der Ansprüche 1 bis 5, worin der organische Träger ein teilweise vernetztes Styrolpolymeres ist.

7. Trägerkatalysator gemäß einem der Ansprüche 1 bis 6, worin die Übergangsmetallverbindung ausgewählt ist unter Cyclopentadienylverbindungen der Formel (I)



worin M für Ti, Zr, Hf oder V steht;  $C_5R^{1}_{5-m}$  und  $C_5R^{1}_{5-m}$  gleich oder verschieden substituierte Cyclopentadienylringe sind; die Substituenten  $R^1$ , gleich oder voneinander verschieden, Wasserstoff, Alkyl-, Alkenyl-, Aryl-, Alkaryl- oder Aralkylreste mit bis 20 Kohlenstoffatomen bedeuten, welche auch Si- oder Ge-Atome oder Gruppen  $Si(CH_3)_3$  enthalten können, oder auch zwei oder vier Substituenten  $R^1$  einer gleichen Cyclopentadienylgruppe einen oder zwei Ringe mit 4 bis 6 Kohlenstoffatomen bilden können;  $R^2$  für eine Gruppe steht, die zwei Cyclopentadienylringe verbrückt und ausgewählt ist unter  $CR^3_2$ ,  $C_2R^3_4$ ,  $SiR^3_3$ ,  $Si_2R^3_4$ ,  $Ge_2R^3_2$ ,  $Ge_2R^3_4$ ,  $R^3_2SiCR^3_2$ ,  $NR^1$  oder  $PR^1$  mit gleichen oder voneinander verschiedenen Substituenten  $R^3$ , die  $R^1$  bedeuten, oder worin zwei oder vier Substituenten  $R^3$  einen oder zwei Ringe mit 3 bis 6 Kohlenstoffatomen ergeben können; die Substituenten Q, die gleich oder voneinander verschieden sind, Halogen, Wasserstoff, OH, SH,  $R^1$ ,  $OR^1$ ,  $SR^1$ ,  $NR^1_2$  oder  $PR^1_2$  bedeuten; m für 0 oder 1 steht; n für 0 oder 1 steht; wobei es 1 ist, wenn m = 1; p für 2 oder 3 steht.

8. Trägerkatalysator gemäß einem der Ansprüche 1 bis 7, worin die organo-metallische Verbindung des Aluminiums ein Alumoxan ist.

9. Trägerkatalysator gemäß einem der Ansprüche 1 bis 8, worin das Molverhältnis zwischen der organo-metallischen Verbindung des Aluminiums und der Übergangsmetallverbindung zwischen 10 und 500 liegt.

10. Verfahren zur Herstellung eines Trägerkatalysators zur Polymerisation von Olefinen gemäß einem der Ansprüche 1 bis 9, umfassend die folgenden Stufen:

das Kontaktieren in einem inerten Lösungsmittel

(A) eines porösen, organischen Trägers, der funktionalisiert ist mit aktive Wasserstoffatome aufweisenden Gruppen, und

(B) zumindest einer organo-metallischen Verbindung des Aluminiums, die zumindest ein Heteroatom, ausgewählt unter Sauerstoff, Stickstoff und Schwefel, enthält; hiernach das Kontaktieren des so erhaltenen Produkts mit

(C) zumindest einer Verbindung eines Übergangsmetalls, ausgewählt unter denjenigen der Gruppen IVb, Vb oder Vlb des Periodensystems der Elemente, die zumindest einen Liganden vom Cyclopentadienyl-Typ enthält;

und schließlich die Gewinnung des Trägerkatalysators durch Entfernen des Lösungsmittels.

11. Verfahren zur Herstellung eines Trägerkatalysators zur Polymerisation von Olefinen gemäß einem der Ansprüche 1 bis 9, umfassend die folgenden Stufen:

das Kontaktieren in einem inerten Lösungsmittel

(B) zumindest einer organo-metallischen Verbindung des Aluminiums, die zumindest ein Heteroatom, ausgewählt unter Sauerstoff, Stickstoff und Schwefel, enthält, und

(C) zumindest einer Verbindung eines Übergangsmetalls, ausgewählt unter denjenigen der Gruppen IVb, Vb oder Vlb des Periodensystems der Elemente, die zumindest einen Liganden vom Cyclopentadienyl-Typ enthält;

hiernach das Kontaktieren des so erhaltenen Produkts mit

(A) einem porösen, organischen Träger, der mit aktive Wasserstoffatome aufweisenden Gruppen funktionalisiert ist;

und schließlich die Gewinnung des Trägerkatalysators durch Entfernen des Lösungsmittels.

12. Verfahren zur Herstellung eines Trägerkatalysators zur Polymerisation von Olefinen gemäß einem der Ansprüche 1 bis 9, umfassend die folgenden Stufen:

das Kontaktieren in einem inerten Lösungsmittel

(A) eines porösen, organischen Trägers, der funktionalisiert ist mit aktive Wasserstoffatome aufweisenden Gruppen, und

(B) zumindest einer organo-metallischen Verbindung des Aluminiums, die zumindest ein Heteroatom, ausgewählt unter Sauerstoff, Stickstoff und Schwefel, enthält;

das Kontaktieren in einem inerten Lösungsmittel



(B) zumindest einer organo-metallischen Verbindung des Aluminiums, die zumindest ein Heteroatom, ausgewählt unter Sauerstoff, Stickstoff und Schwefel, enthält, und

(C) zumindest einer Verbindung eines Übergangsmetalls, ausgewählt unter denjenigen der Gruppen IVb, Vb oder VIb des Periodensystems der Elemente, die zumindest einen Liganden vom Cyclopentadienyl-Typ enthält;

hiernach das Kontaktieren des Produkts, das erhalten wurde durch Kontaktieren von (A) und (B) mit dem durch Kontaktieren von (B) und (C) erhaltenen Produkt;

und schließlich die Gewinnung des Trägerkatalysators durch Entfernen des Lösungsmittels.

13. Verfahren gemäß einem der Ansprüche 10 bis 12, worin der organische Träger pre-kontaktiert wird mit zumindest einer Aluminiumalkylverbindung der Formel (VI)



worin  $R^5$  unter Alkyl-, Alkenyl-, Aryl-, Alkaryl- und Aralkylresten mit 1 bis 10 Kohlenstoffatomen ausgewählt ist, X unter Wasserstoff- und Halogenatomen ausgewählt ist, q für eine ganze Zahl zwischen 1 und 3 steht.

14. Verfahren gemäß Anspruch 13, worin die Aluminiumalkylverbindung Triisobutylaluminium ist.

15. Trägergestützter und pre-polymerisierter Katalysator zur Polymerisation von Olefinen, erhältlich durch Unterwerfen eines Trägerkatalysators gemäß einem der Ansprüche 1 bis 9 einer Pre-Polymerisationsbehandlung mit zumindest einem olefinischen Monomeren.

16. Trägergestützter und pre-polymerisierter Katalysator gemäß Anspruch 15, worin die Menge des gebildeten Polymeren zwischen 0,5 und 10 Gew. Teilen, bezogen auf das Gewicht des Trägerkatalysators, beträgt.

17. Trägergestützter und pre-polymerisierter Katalysator gemäß einem der Ansprüche 15 oder 16, umfassend eine Alkylaluminiumverbindung der Formel (VI)



worin  $R^5$ , X und q wie vorstehend definiert sind.

18. Verfahren zur Homo- oder Copolymerisation von Olefinen, umfassend die Polymerisationsreaktion eines oder mehrerer olefinischer Monomere in Anwesenheit eines Trägerkatalysators gemäß einem der Ansprüche 1 bis 9.

19. Verfahren zur Homo- oder Copolymerisation von Olefinen, umfassend die Polymerisationsreaktion eines oder mehrerer olefinischer Monomere in Anwesenheit eines trägergestützten und pre-polymerisierten Katalysators gemäß einem der Ansprüche 15 bis 17.

20. Verfahren zur Homo- oder Copolymerisation von Olefinen gemäß einem der Ansprüche 18 oder 19, worin der Katalysator pre-kontaktiert wird mit zumindest einer Verbindung, ausgewählt unter den Alkylaluminiumverbindungen der Formel (VI)



worin  $R^5$ , X und q wie vorstehend definiert sind, und den organo-metallischen Verbindungen des Aluminiums, die zumindest ein Heteroatom, ausgewählt unter Sauerstoff, Stickstoff und Schwefel, enthalten.

21. Verfahren zur Homo- oder Copolymerisation von Olefinen gemäß Anspruch 20, worin die organo-metallische Verbindung des Aluminiums Alumoxane sind.

## Revendications

1. Un catalyseur supporté pour la polymérisation d'oléfines comprenant :

- (A) un support organique poreux fonctionnalisé par des groupes ayant des atomes d'hydrogène actif ;  
 (B) au moins un dérivé organométallique de l'aluminium contenant au moins un hétéroatome choisi parmi l'oxygène, l'azote et le soufre ; et  
 (C) au moins un dérivé d'un métal de transition choisi parmi ceux du groupe IVb, Vb ou Vlb du tableau périodique des éléments, contenant au moins un ligand du type cyclopentadiényle.

2. Le catalyseur supporté selon la revendication 1, dans lequel le support organique présente une porosité supérieure à 0,2 cm<sup>3</sup>/g et une surface spécifique supérieure à 30 m<sup>2</sup>/g.

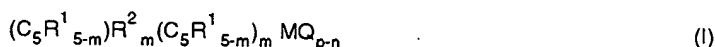
3. Le catalyseur supporté selon l'une quelconque des revendications 1 ou 2, dans lequel le support organique est sous la forme de particules présentant une morphologie microsphéroïdale et un diamètre compris entre 5 et 1000 µm.

4. Le catalyseur supporté selon l'une quelconque des revendications 1 à 3, dans lequel les groupes fonctionnels du support organique sont choisis parmi les groupes hydroxy, amino primaire, amino secondaire, sulfonique, carboxylique, amido, amido-N-monosubstitué, sulfonamido, sulfonamido-N-monosubstitué, sulphdryle, imido et hydrazido.

5. Le catalyseur supporté selon l'une quelconque des revendications 1 à 4, contenant une quantité de groupes fonctionnels supérieure à 0,2 milliéquivalent pour chaque gramme de support solide.

6. Le catalyseur supporté selon l'une quelconque des revendications 1 à 5, dans lequel le support organique est un polymère styrénique partiellement réticulé.

7. Le catalyseur supporté selon l'une quelconque des revendications 1 à 6, dans lequel le dérivé de métal de transition est choisi parmi les dérivés cyclopentadiényles de formule (I) :



dans laquelle :

M est Ti, Zr, Hf ou V ;

les groupes  $C_5R^1_{5-m}$  sont des cycles cyclopentadiényle identiquement ou différemment substitués ; les substituants  $R^1$ , identiques ou différents, sont des hydrogènes ou des radicaux alkyle, alkényle, aryle, alkaryle ou aralkyle comportant 1 à 20 atomes de carbone, qui peuvent également comporter des atomes de Si ou de Ge, ou des groupes  $Si(CH_3)_3$ , ou encore, deux ou quatre substituants  $R^1$  d'un même groupe cyclopentadiényle peuvent former un ou deux cycles comportant 4 à 6 atomes de carbone ;  $R^2$  est un groupe qui lie par pontage les deux cycles cyclopentadiényle et qui est choisi parmi  $CR^3_2$ ,  $C_2R^3_4$ ,  $SiR^3_3$ ,  $Si_2R^3_4$ ,  $GeR^3_2$ ,  $GeR^3_4$ ,  $R^3_2SiCR^3_2$ ,  $NR^1$  ou  $PR^1$ , avec des substituants  $R^3$  identiques ou différents les uns des autres, qui sont  $R^1$  ou bien deux ou quatre substituants  $R^1$  peuvent former un ou deux cycles comportant 3 à 6 atomes de carbone ; les substituants Q, identiques ou différents les uns des autres, sont halogène, des hydrogène, OH, SH,  $R^1$ ,  $OR^1$ ,  $SR^1$ ,  $NR^1_2$  ou  $PR^1_2$  ;

m est égal à 0 ou 1 ;

n est égal à 0 ou 1 ; et étant égal à 1 quand m=1 ;

p est égal à 2 ou 3.

8. Le catalyseur supporté selon l'une quelconque des revendications 1 à 7, dans lequel le dérivé organométallique de l'aluminium est un alumoxane.

9. Le catalyseur supporté selon l'une quelconque des revendications 1 à 8, dans lequel le rapport molaire entre le dérivé organométallique de l'aluminium et le dérivé de métal de transition est compris entre 10 et 500.

10. Un procédé de préparation d'un catalyseur supporté pour la polymérisation d'oléfines selon l'une quelconque des revendications 1 à 9, comprenant les étapes de :  
mise en contact dans un solvant inerte :

(A) d'un support organique poreux fonctionnalisé par des groupes ayant des atomes d'hydrogène actif ; et  
(B) d'au moins un dérivé organométallique de l'aluminium contenant au moins un hétéroatome choisi parmi oxygène, azote et soufre ;

suivie de la mise en contact du produit ainsi obtenu avec

(C) au moins un dérivé d'un métal de transition choisi parmi ceux des groupes IVb, Vb ou VIb du tableau périodique des éléments, contenant au moins un ligand du groupe cyclopentadiényle ;  
et enfin isolement du catalyseur supporté en éliminant le solvant.

11. Un procédé de préparation d'un catalyseur supporté pour la polymérisation d'oléfines selon l'une quelconque des revendications 1 à 9, comprenant les étapes de :  
mise en contact dans un solvant inerte

(B) d'au moins un dérivé organométallique de l'aluminium contenant au moins un hétéroatome choisi parmi l'oxygène, l'azote et le soufre ; et

(C) d'au moins un dérivé d'un métal de transition choisi parmi ceux des groupes IVb, Vb ou VIb du tableau périodique des éléments, contenant au moins un ligand du type cyclopentadiényle ;

suivies de la mise en contact du produit ainsi obtenu avec :

(A) un support organique poreux fonctionnalisé par des groupes ayant des atomes d'hydrogène actif ;  
et enfin isolement du catalyseur supporté en éliminant le solvant.

12. Un procédé de préparation d'un catalyseur supporté pour la polymérisation d'oléfines selon l'une quelconque des revendications 1 à 9, comprenant les étapes de :  
mise en contact dans un solvant inerte :

(A) d'un support organique poreux fonctionnalisé par des groupes ayant des atomes d'hydrogène actif ; et

(B) d'au moins un dérivé organométallique d'aluminium contenant au moins un hétéroatome choisi parmi oxygène, azote et soufre ;

mise au contact dans un solvant inerte :

(B) d'au moins un dérivé organométallique de l'aluminium contenant au moins un hétéroatome choisi parmi oxygène, azote et soufre ; et

(C) au moins un dérivé d'un métal de transition choisi parmi ceux des groupes IVb, Vb ou VIb du tableau périodique des éléments, contenant au moins un ligand du type cyclopentadiényle ;

puis mise en contact du produit obtenu par la mise en contact de (A) et (B) avec le produit obtenu par la mise en contact de (B) et (C) ;

et enfin isolement du catalyseur supporté en éliminant le solvant.

13. Le procédé selon l'une quelconque des revendications 10 à 12, dans lequel le support organique préalablement mis en contact avec au moins un dérivé d'alkylaluminium de formule (VI) :



dans laquelle :

$R^5$  est choisi parmi les radicaux alkyle, alkényle, aryle, alkaryle et aralkyle comportant de 1 à 10 atomes de carbone ;

X est choisi parmi les atomes d'hydrogène et d'halogène ; et

q est un nombre entier compris entre 1 et 3.

14. Le procédé selon la revendication 13, dans lequel le dérivé alkylaluminium est le triisobutylaluminium.
15. Un catalyseur supporté et prépolymérisé pour la polymérisation d'oléfines susceptible d'être obtenu en soumettant un catalyseur supporté selon l'une quelconque des revendications 1 à 9 à un traitement de prépolymérisation à l'aide d'au moins un monomère oléfinique.
16. Un catalyseur supporté et prépolymérisé selon la revendication 15, dans lequel la quantité de polymère produite est comprise entre environ 0,5 et 10 parties en poids par rapport au poids du catalyseur supporté.
17. Le catalyseur supporté et prépolymérisé selon l'une quelconque des revendications 15 ou 16, comprenant un dérivé alkylaluminium de formule (VI) :



dans laquelle  $R^5$ , X et q sont tels que définis ci-dessus.

18. Un procédé d'homo- ou de co-polymérisation d'oléfines comprenant la réaction de polymérisation d'un ou plusieurs monomères oléfiniques en présence d'un catalyseur supporté selon l'une quelconque des revendications 1 à 9.
19. Un procédé d'homo- ou de co-polymérisation d'oléfines comprenant la réaction de polymérisation d'un ou plusieurs monomères oléfiniques en présence d'un catalyseur supporté et prépolymérisé selon l'une quelconque des revendications 15 à 17.
20. Un procédé d'homo- ou de co-polymérisation d'oléfines selon l'une quelconque des revendications 18 ou 19, dans lequel le catalyseur est mis en contact préalablement avec au moins un dérivé choisi parmi les dérivés alkylaluminium de formule (VI) :



dans laquelle  $R^5$ , X et q sont tels que définis ci-dessus, et le dérivé organométallique de l'aluminium contenant au moins un hétéroatome choisi parmi oxygène, azote et soufre.

21. Le procédé d'homo- ou de co-polymérisation d'oléfines selon la revendication 20, dans lequel le dérivé organométallique de l'aluminium est un alumoxane.